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EPA METHOD STUDY 21, METHOD 611--HALOETHERS

by

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16. ABSTRACT

Described herein are the experimental design and the results of an interlaboratory study of an analytical method to detect haloethers in water. The method, EPA Method 611 - Haloethers, consisted of a liquid/liquid extraction using methylene chloride, an evaporation step using Kuderna-Danish (K-D) evaporators, a cleanup procedure using Florisil sorbent, another K-D evaporation of the fraction from the Florisil column, and subsequent analysis by gas chromatography using a halide-specific detector. The six concentration (three Youden pairs) of spiking solutions used in this study contained bis (2-chloroisopropyl) ether, bis(2-chloroethyl) ether, bis(2-chloroethyoxy) methane, 4-chlorophenyl phenyl ether, and 4-bromophenyl phenyl ether. Six water types were used in the study: distilled, tap, surface, and three different industrial wastewaters. Statistical analysis and conclusions in this report are based on analytical data obtained by 20 collaborating laboratories.

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory (EMSL)-Cincinnati research responsibilities are to:

- Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria, and other microorganisms in water.
- Conduct studies to determine the responses of aquatic organisms to water quality.
- Conduct an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

This publication reports the results of EPA's interlaboratory method study for *bis*(2-chloroisopropyl)ether (BCIPE), *bis*(2-chloroethyl)ether (BCEE),*bis*(2-chloroethoxy)methane (BCEXM), 4-chlorophenyl phenyl ether (CPPE), 4-bromophenyl phenyl ether (BPPE). Federal agencies, states, municipalities, universities, private laboratories, and industry should find this interlaboratory study useful in monitoring and controlling pollution in the environment.

Robert L. Booth, Director
Environmental Monitoring and Support Laboratory

ABSTRACT

This report describes the interlaboratory study of an analytical method which detects haloethers in water. EPA Method 611 -- Haloethers, consists of a liquid/liquid extraction using methylene chloride, an evaporation step using Kuderna-Danish (K-D) evaporators, a cleanup procedure using Florisil sorbent, another K-D evaporation of the fraction from the Florisil column, and subsequent analysis by gas chromatography (GC) using a halide-specific detector. The six concentrations (three Youden pairs) of spiking solutions used in this study contained BCIPE, BCEE, and BCEXM, CPEE, and BPPE. Six water types were used in the study: distilled, tap, surface, and three different industrial wastewaters. Statistical analyses and conclusions in this report are based on analytical data obtained by 20 collaborating laboratories.

Participating laboratories were selected based upon technical evaluation of proposals and upon the analytical results of pre-study samples. The data obtained from the interlaboratory study were analyzed employing EPA's series of computer programs known as the Interlaboratory Method Validation Study (IMVS) system, which basically implements ASTM Standard D 2777. The statistical analyses included tests for the rejection of outliers, estimation of mean recovery (accuracy), estimation of single-analyst and overall precision, and tests for the effects of water type on accuracy and precision.

This report was submitted in fulfillment of Contract 68-03-2633 by Monsanto Company under the sponsorship of the U.S. Environmental Protection Agency and covers a period from January 1979 to March 1980.

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SECTION 1

INTRODUCTION

The EPA's analytical laboratories gather water quality data to provide information on water resources, to assist research activities, and to evaluate pollution abatement activities. The success of the Agency's pollution control activities, particularly when legal action is involved, depends upon the reliability of the data provided by the laboratories.

Under provisions of the Clean Water Act, the EPA promulgates guidelines establishing test procedures for the analysis of pollutants. The Clean Water Act Amendments of 1977 emphasize the control of toxic pollutants and declare the 65 "priority" pollutants and classes of pollutants to be toxic under Section 307(a) of the Act. This report is one of a series that investigates the analytical behavior of selected priority pollutants and suggests a suitable test procedure for their measurement. The priority pollutants analyzed by Method 611 in this report are the study haloethers: BCIPE, BCEE, BCEXM, CPPE and BPPE.

EMSL-Cincinnati develops analytical methods and conducts a quality assurance program for water laboratories to maximize the reliability and legal defensibility of water quality information collected by EPA laboratories. This responsibility is assigned to the Quality Assurance Branch (QAB) which conducts interlaboratory studies on the methods in order to generate precision and accuracy data. This report presents the results of interlaboratory study 21, conducted for the USEPA by the prime contractor; Monsanto Company (MC).

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Monsanto Company conducted the study in three phases. Phase I involved the analysis of the prestudy samples by 20 participating laboratories. Two samples were analyzed for each of the five haloethers. A medium concentration sample was analyzed in distilled water supplied by the participating laboratories and a low level sample was analyzed in a wastewater sample supplied by MC. The objective of Phase I was to familiarize laboratories with Method 611 and to identify potential problems associated with the analytical methodology. A short report, including the data obtained and any potential problems encountered, was received from each subcontracting laboratory by MC at the completion of Phase I.

Phase II consisted of a prestudy conference held at EMSL-Cincinatti, on May 16, 1979 to which each subcontracting laboratory sent at least one participant. The prestudy conference was designed to examine the results of Phase I and to discuss any problems encountered in the methodology.

Phase III was the formal interlaboratory study. Five haloethers were analyzed at six concentrations (three Youden pairs) in six different water matrices. Each participating laboratory supplied its own reagent grade water, tap water and surface water. MC supplied the three industrial wastewaters. In addition, the participating laboratories performed analyses of all water blanks with no spiked compounds. Each participating laboratory then issued a report to Monsanto Company containing all data obtained, copies of all chromatograms, and comments.

The final step in the study was a statistical analysis of data by Battelle Columbus Laboratories, Columbus, Ohio, under contract 68-03-2624 employing U.S. EPA's IMVS computer programs.

SECTION 2

CONCLUSIONS

The object of this study was to characterize the performance of Method 611 in terms of accuracy, overall precision, single-analyst precision and the effect of water types on accuracy and precision. Through statistical analyses of 3,600 analytical values, estimates of accuracy and precision were made and expressed as regression equations, which are shown in Table 1. One measure of the performance of the method is that 16.3% of the analytical values were rejected as outliers. Of these, 6.1% were rejected through application of Youden's laboratory ranking procedure and 10.2% were rejected employing the Thompson-T-test.

The accuracy of the method is obtained by comparing the mean recovery to the true values of the concentration. It is expressed as percent recovery and ranges from 56% to 85% for all five analytes in all six water.

The overall standard deviation indicates the precision associated with measurements generated by a group of laboratories. The percent relative standard deviation (% RSD) ranges from 32% to 53%.

The single-analyst standard deviation indicates the precision associated within a single laboratory. The percent relative standard deviation for a single analyst (% RSD-SA) ranges from 15% to 31%.

A statistical comparison of the effect of water type was performed indicating a statistically significant difference for six of the

analyte/water matrix combinations. Of these six cases, a practical significant difference was established only for 4-chlorophenyl phenyl ether in wastewater 2. This combination also exhibited the lowest accuracy and highest precision (lowest % RSD and RSD-SA) values of all 30 analyte/water pairs.

In general, the slopes of the regression equations presented in Table 1 provided an excellent fit to the data especially in the middle and high Youden concentrations pairs. Recovery and precision data at the lowest concentrations suffered from a lack of detection sensitivity and from the presence of background interferences in the blank samples. The fit of the regression equations for accuracy and precision reinforces the assumption that percent recovery is independent of concentration and that absolute recovery is a linear function of the analyte concentration.

A detailed examination of the data indicated a background interference problem for wastewater 2 where the recoveries for the low Youden pairs were 541% and 442% for BCEE, and 46% and 287% for 4-CPPE. For this reason a new set of linear regression equations were generated omitting the low Youden pair data. The revised regression equations for BCEE and 4-CPPE in wastewater 2 are presented in Table 2.

In preliminary studies by the prime contractor, it was found that each of the haloether compounds responded best to the Hall 310 detector at different temperatures. It was therefore necessary to find a compromise reactor temperature that gave good response for all five compounds. The newer Hall detectors use metallic reactor tubes rather than quartz tubes. These metallic tubes are said to have a catalytic effect which eliminates the need for such critical temperature selection.

TABLE 1. REGRESSION EQUATIONS FOR ACCURACY AND PRECISION

WATER TYPE	BIS(2-CHLOROISOPROPYL)ETH	BIS(2-CHLOROETHYL)ETHER	BIS(2-CHLOROETHOXY)METHAN	4-CHLOROPHENYL PHENYL ETH
APPLICABLE CONC. RANGE	(2.40 - 624.00)	(1.40 - 602.00)	(1.00 - 528.00)	(6.60 - 489.00)
DISTILLED WATER				
SINGLE-ANALYST PRECISION	SR = 0.20X + 1.05	SR = 0.19X + 0.28	SR = 0.20X + 0.15	SR = 0.18X + 2.13
OVERALL PRECISION	S = 0.36X + 0.79	S = 0.35X + 0.36	S = 0.33X + 0.11	S = 0.41X + 0.55
ACCURACY	X = 0.85C + 1.67	X = 0.81C + 0.54	X = 0.71C + 0.13	X = 0.82C + 1.97
TAP WATER				
SINGLE-ANALYST PRECISION	SR = 0.15X + 0.03	SR = 0.18X + 0.25	SR = 0.21X + 0.21	SR = 0.17X + 1.22
OVERALL PRECISION	S = 0.36X + 0.55	S = 0.40X + 0.18	S = 0.38X + 0.69	S = 0.39X + 0.78
ACCURACY	X = 0.78C + 0.99	X = 0.72C + 0.48	X = 0.67C + 0.69	X = 0.75C + 0.63
SURFACE WATER				
SINGLE-ANALYST PRECISION	SR = 0.29X + 0.77	SR = 0.27X - 0.06	SR = 0.29X - 0.08	SR = 0.22X + 0.83
OVERALL PRECISION	S = 0.47X + 0.23	S = 0.50X + 0.09	S = 0.53X + 0.47	S = 0.42X + 0.14
ACCURACY	X = 0.77C + 0.42	X = 0.67C + 0.39	X = 0.60C + 0.74	X = 0.67C + 1.14
WASTE WATER 1				
SINGLE-ANALYST PRECISION	SR = 0.24X + 0.15	SR = 0.26X + 0.07	SR = 0.23X + 0.43	SR = 0.25X + 0.78
OVERALL PRECISION	S = 0.40X + 1.93	S = 0.41X + 0.06	S = 0.48X + 0.54	S = 0.43X + 0.40
ACCURACY	X = 0.73C + 2.00	X = 0.69C + 0.25	X = 0.69C + 0.69	X = 0.65C + 0.97
WASTE WATER 2				
SINGLE-ANALYST PRECISION	SR = 0.29X + 0.09	SR = 0.15X + 2.26	SR = 0.22X + 1.37	SR = 0.15X +15.99
OVERALL PRECISION	S = 0.52X + 1.00	S = 0.35X + 4.12	S = 0.34X + 2.10	S = 0.32X +17.01
ACCURACY	X = 0.83C + 1.66	X = 0.72C + 7.77	X = 0.71C + 2.33	X = 0.56C +20.40
WASTE WATER 3				
SINGLE-ANALYST PRECISION	SR = 0.28X + 0.22	SR = 0.23X + 0.04	SR = 0.26X + 0.18	SR = 0.28X + 0.89
OVERALL PRECISION	S = 0.42X + 0.33	S = 0.41X + 0.06	S = 0.36X + 0.70	S = 0.38X + 0.97
ACCURACY	X = 0.80C + 0.39	X = 0.72C + 0.14	X = 0.67C + 0.97	X = 0.69C + 1.51

X = MEAN RECOVERY
C = TRUE VALUE FOR THE CONCENTRATION

TABLE 1 (continued)

WATER TYPE	4-BROMOPHENYL PHENYL ETHE
APPLICABLE CONC. RANGE	(2.80 - 626.00)
DISTILLED WATER	
SINGLE-ANALYST PRECISION	SR = 0.25X + 0.21
OVERALL PRECISION	S = 0.47X + 0.37
ACCURACY	X = 0.85C + 2.55
TAP WATER	
SINGLE-ANALYST PRECISION	SR = 0.22X + 0.33
OVERALL PRECISION	S = 0.47X + 0.52
ACCURACY	X = 0.82C + 1.87
SURFACE WATER	
SINGLE-ANALYST PRECISION	SR = 0.27X + 0.59
OVERALL PRECISION	S = 0.49X + 0.47
ACCURACY	X = 0.78C + 2.10
WASTE WATER 1	
SINGLE-ANALYST PRECISION	SR = 0.30X + 0.33
OVERALL PRECISION	S = 0.48X + 0.61
ACCURACY	X = 0.77C + 2.16
WASTE WATER 2	
SINGLE-ANALYST PRECISION	SR = 0.29X + 1.26
OVERALL PRECISION	S = 0.51X + 0.45
ACCURACY	X = 0.81C + 2.30
WASTE WATER 3	
SINGLE-ANALYST PRECISION	SR = 0.31X + 0.13
OVERALL PRECISION	S = 0.47X + 0.22
ACCURACY	X = 0.79C + 1.68

X = MEAN RECOVERY
C = TRUE VALUE FOR THE CONCENTRATION

TABLE 2. REVISED LINEAR REGRESSION EQUATIONS FOR WASTEWATER 2

	BCEE	4-CPPE
Single-Analyst Precision	SR = 0.10X - 3.47	SR = 0.11X + 6.00
Overall Precision	$\bar{S}$ = 0.39X - 2.26	$\bar{S}$ = 0.49X - 8.98
Accuracy	$\bar{X}$ = 0.72C + 8.61	$\bar{X}$ = 0.69C + 9.75

A preliminary study of eight different effluent/wastewaters was conducted to determine the effectiveness of the method in eliminating potential interferences to the analysis of haloethers and identifying some of the remaining interferences. This study vividly demonstrated the effectiveness of the Florisil cleanup in removing potential interferences. In many cases, very large potential interferences observed in samples after extraction and concentration were totally eliminated by the Florisil cleanup. A gas chromatographic/mass spectrometric (GC/MS) analysis of samples after cleanup also identified a number of compounds which were not observed in the halide-specific detector chromatograms. Compounds identified in the wastewaters as posing interference problems included a nonpriority pollutant haloether and a cyclic chlorinated hydrocarbon. Large quantities of nonhalogen containing hydrocarbons were also found to give a response, though greatly reduced, with the halide-specific detectors. Minor changes in chromatographic conditions were generally able to separate potential interferences from the haloethers even with the worst case wastewater used. In final discharge waters, it is not anticipated that interferences will pose a significant problem in the analysis of haloethers with this method.

In general, the most sensitive portion of the method is the Kuderna-Danish concentration step. It requires some analyst care and experience to conduct this concentration step in a reproducible manner.

SECTION 3

RECOMMENDATIONS

Method 611 is recommended for the analysis of haloethers in municipal and industrial wastewaters. The matrix effects are significant only at low concentration levels.

Care should be taken in the Florisil cleanup and K-D concentration steps. Analyst care and experience is required to conduct the concentration step in a reproducible manner.

Special care should be taken to break the emulsions developing in the extraction step of the analysis to prevent loss of analyte.

SECTION 4

DESCRIPTION OF STUDY

SELECTION OF PARTICIPATING LABORATORIES

As prime contractor, Monsanto Company sent requests for quotation (RFQ) to approximately 150 laboratories which had been identified as potential subcontractors for this interlaboratory study. The RFQ contained a Scope of Work, a description of the projected timing of the required analyses, and a copy of the analytical method. The detailed writeup for Method 611 as published by EPA is presented in Appendix A of this report. Interested laboratories were asked to respond to the RFQ by providing the following information on:

- Facilities available at the laboratory, including all instrumentation to be used for the study.
- Previous experience in carrying out the types of analyses specified in the Scope of Work for the compounds of interest.
- Handling procedures for working with hazardous and potentially hazardous chemicals.
- The organization and managerial structure of the laboratory, identifying those personnel involved in managing this study.
- The analyst involved in the analyses to be performed, including his/her experience.

- Quality control/quality assurance procedures and good laboratory practices followed by the laboratory.

Approximately 30 proposals were received in response to the RFQ. The proposals received were ranked, and the 20 most qualified laboratories were selected for participation. Table 3 lists the participating laboratories for the Method 611 interlaboratory study. Throughout this report, data provided by these laboratories will be identified only by an anonymous code number.

STUDY DESIGN

Two preliminary samples were sent to the participating laboratories. One was supplied at a medium level to be analyzed in distilled water to assure that the method could be properly implemented. The second sample was at a low level to be spiked into a liter of wastewater that was supplied. This sample was to find the method problems under adverse conditions.

The analysts from these laboratories met in Cincinnati on May 16, 1979 to discuss the procedures and potential problems. The discussion included elements dealing with problems in achieving low enough detection limits, the necessity of Florisil standardization per the Federal Register method, reactor tube composition, and other questions as to which elements of the study were fixed and which elements could be optimized by the individual laboratories. About a month after the prestudy conference, agreement was reached by the EPA and MC concerning which components were to be rigidly fixed. The method study samples and wastewaters were then sent to the laboratories.

Rigidly set conditions included the specifications of column packing material, again excluding EC detectors as not being halogen specific, and specifying that the Federal Register method be

TABLE 3. PARTICIPATING LABORATORIES

Analytical Development Co.
1875 Willow Park Way
Monument, Colorado 80132

Analytical Research Laboratories, Inc.
160 Taylor Street
Monrovia, California 91016

Battelle (Columbus Laboratories)
505 King Avenue
Columbus, Ohio 43201

CDM Environmental Sciences Division
6132 West Fond du Lac Avenue
Milwaukee, Wisconsin 53218

Environmental Research and Technology
2625 Lowingate Road
Westlake Village,
California 91361

Environmental Research and Technology
696 Virginia Road
Concord, Massachusetts 01742

Environmental Research Group
117 North First
Ann Arbor, Michigan 48103

Environmental Science and Engineering
P.O. Box 13454
Gainesville, Florida 32604

Finnigan Institute
11750 Chesterdale Road
Cincinnati, Ohio 45246

Hydrosciences, Incorporated
363 Olk Hood Road
Westwood, New Jersey 07675

New Mexico Scientific Laboratory Systems
700 Camino de Salud
Albuquerque, New Mexico 87106

Orlando Laboratories, Inc.
90 West Jersey Street
Orlando, Florida 32856

Raltek Science Services
3301 Kinsman Boulevard
Madison, Wisconsin 53707

Southwest Research Institute
8500 Culebra Road
San Antonio, Texas 78284

Spectrix Corporation
7408 Fannin
Houston, Texas 77054

Texas Instruments, Inc.
P.O. Box 5621-MS 949
Dallas, Texas 75265

Versar, Inc.
6621 Electronic Drive
Springfield, Virginia 22151

Water and Air Research, Inc.
P. O. Box 52329
Jacksonville, Florida 32201

West Coast Technical Service
17605 Fabrica Way
Cerritos, California 90701

Wilson Laboratories
528 North 9th Street
Salina, Kansas 67401

followed in detail. The temperature program, flow rates, and solvent compositions were given as guidelines only since a variety of detectors were being used.

Suggested guidelines were also given for parameters such as furnace temperature on the Hall electrolytic conductivity detectors. MC has used a Hall 310 detector for many analyses and it was found the sensitivity of the detector varied significantly as a function of the temperature and differed from compound to compound. Only two of the 20 laboratories, however, used this detector. Because a wide variety of detectors were used in the study, a great deal of flexibility was allowed for individual optimization of the instrument conditions described within the scope of the Federal Register method.

Three industrial wastewaters were selected for the interlaboratory study. Each wastewater was obtained from a different chemical company which either produces haloethers or had the potential of haloether byproducts in the production of other chemicals. Wastewaters #1 and #2 were raw effluents before treatment, and wastewater #3 was diluted effluent destined for deep well injection. These were selected as worst case examples to evaluate the method in the presence of the types of interferences which might be expected by NPDES permit holders analyzing for haloethers. The final treated discharge waters would generally have lower levels of these interferences. Wastewater #2 contained the most significant quantities of interfering compounds.

Each wastewater was thoroughly mixed, filtered, and dispensed in one liter Weaton bottles equipped with Teflon lid liners. Each of the participating laboratories was sent seven one liter bottles of each wastewater. Six of these bottles were each spiked with one of the six spiking solutions, while the seventh bottle served as the blank.

In addition to the three wastewaters, each laboratory supplied its own tap water, reagent grade water, and surface water samples. After spiking, each laboratory had 42 different samples (including blanks), for analysis.

The study design was based on Youden's non-replicate plan [1] for collaborative evaluation of precision and accuracy for analytical methods. According to Youden's design, samples are analyzed in pairs, each sample of a pair with slightly different concentrations of the constituents. The analyst is directed to do a single analysis and report one value for each sample. Analyses in reagent grade water evaluated the proficiency of the analyst to use the method on a sample free of interferences; analyses in the other waters were intended to reveal the effects of interferences on the method.

Six spiking solutions were made such that three different concentration ranges were each represented by two different solutions (Youden pairs). Solution numbers 1 and 5 had haloether concentrations near the minimum detectable limits. Solution numbers 2 and 6 had concentrations around 100 ppb. Solution numbers 3 and 4 contained haloethers at levels about five times the intermediate levels. Table 4 shows the individual haloether concentrations for each spiking solution.

A problem with CPPE occurred when the solutions were made. CPPE was purchased in sealed glass ampules containing 10, 20, or 50 mg of CPPE. It was assumed that the weight listed on the label was a precise weight, so the contents were simply rinsed into the spiking solutions. Initial analyses of the solutions showed considerable discrepancy between the "theoretical" concentrations and the analyzed values for CPPE. Subsequent ampules were checked for actual weights, and it was found that they normally contained much more than the stated weight. A check with the supplier confirmed that

TABLE 4. SPIKING SOLUTION CONCENTRATIONS

Solution	Concentration, µg/mL				
	BCIPE	BCEE	BCEXM	CPPE	BPPE
#1	3.0	1.4	1.4	14.5	2.8
#2	132	108	106	94	145
#3	486	602	398	489	552
#4	624	402	528	424	626
#5	2.4	1.6	1.0	6.6	3.8
#6	92	87	126	120	116

the stated weights were intended as approximations showing the minimum weight. The collaborating laboratories were informed of this potential source of error when making their own standards. The initial analytical values determined in triplicate by direct injection were used as the true values for CPPE for this study.

The spiking solutions were heat sealed in 5-mL hard glass ampules. Each ampule contained 1.5 mL of solution, of which 1.0 mL was used to spike a liter of water. To prevent loss of analyte or acetone solvent, the ampules were cooled under a liquid nitrogen stream while being sealed. The ampules were refrigerated until used or were sent to the subcontract laboratories. Each laboratory was then sent a set of spiking solutions containing six ampules of each of the six solutions.

In the methods development phase of this program, stability studies were conducted by MC to select the optimum solvent for preparation of the spiking solutions. Acetone was selected as the solvent and it was determined that the haloethers were stable up to 90 days. The spiking solutions for the validation study were prepared well in advance of the time they would be used, and the turnaround time of the participating laboratories was long; therefore, it

was decided to analyze all the solutions at about the same time the 20 laboratories were using them in addition to the shorter term (90 day) stability tests. In this way, it could be assured that haloether degradation or losses would not contribute to variations in data from the various laboratories. The additional analyses for stability of the spiking solutions were conducted 230 days after the solutions were made. Even after 230 days, the spiking solutions were stable.

MC interacted with all of the laboratories involved in the study. This interaction varied from verbal discussions of the potential problems of analysis to sending a MC employee to five laboratories to assist in troubleshooting. The major difficulties encountered were interfacing the Hall detectors to a wide variety of gas chromatographs and lack of proper sensitivity.

At the conclusion of the study, a questionnaire was sent to each of the participating laboratories requesting information on the operating conditions used for the analyses, problems encountered with the method, and any other variables associated with the conduct of the method, for example, how emulsions were broken in the methylene chloride separations. Comparisons of the detector type to the quality of results obtained showed little correlation. Initial feelings were that the Hall 700A detector would produce superior results to the Hall 700 and Hall 310 detectors, but this was not found to be significant. Users of detectors other than the Hall models said their detectors had nonlinear responses. The data generated, however, were similar in quality to the Hall detector data.

The raw data reported by the 20 laboratories are presented in Appendix B of this report. The values reported have been corrected for the blank values. The asterisked pieces of data were rejected as outliers for further statistical analysis. Details of the methods for detection of outliers are presented in Section 5 of this report.

SECTION 5

STATISTICAL TREATMENT OF DATA

Data obtained from the interlaboratory study were subjected to statistical analyses by the Battelle Columbus Laboratories, Columbus, Ohio, under EPA Contract 68-03-2624. The analyses were performed employing EPA's Interlaboratory Method Validation Study (IMVS) system [2] of computer programs which was designed to implement ASTM procedure D2777, "Standard Practice for Determination of Precision and Bias of Methods of Committee D-19 on Water" [3]. The analyses conducted using the IMVS system included tests for the rejection of outliers (both whole laboratories for a water type and individual data points), estimation of mean recovery (accuracy), estimation of single-analyst and overall precision, and tests for the effects of water type on accuracy and precision.

REJECTION OF OUTLIERS

An outlying observation, or "outlier," is a data point that appears to deviate markedly from other members of the sample in which it occurs. Outlying data points are very commonly encountered during interlaboratory test programs. If they are not removed, they can result in a distortion of the accuracy and precision statistics which characterize the analytical method. These outlying points cannot be removed indiscriminantly, however, because they may represent an extreme manifestation of the random variability inherent in the method.

ASTM procedure E178-80, "Standard Practice for Dealing with Outlying Observations," [4] and ASTM procedure D2777-77 [3] present explicit statistical rules and methods for identification of outliers.

Data from outlying laboratories for a particular water type were rejected employing Youden's laboratory ranking test procedure [3, 5] at the 5% level of significance. Data remaining after the laboratory ranking procedure were subjected to individual outlier tests. After zero, missing, "less than" and "nondetect" data were rejected as outliers, the average and standard deviation for the remaining data were calculated. The remaining data were examined for additional outliers employing the outlier rejection test constructed by Thompson [6]. Data rejected as outliers for this study are identified by an asterisk in the tables of raw data shown in Appendix B.

Youden's Laboratory Ranking Procedure

Using the data for each water type, Youden's laboratory ranking test [3, 5] was performed at the 5% level of significance. The Youden laboratory ranking procedure requires a complete set of data from each laboratory within each water type. Missing data from laboratory "i" for water type "j" were replaced by the following procedure. Letting X_{ijk} denote the reported measurement from laboratory "i" for water type "j" and concentration level C_k, it is assumed that

$$X_{ijk} = \beta_j \cdot C_k^{\gamma_j} \cdot L_i \cdot \varepsilon_{ijk} \qquad (1)$$

where β_j and γ_j are fixed parameters which determine the effect of water type "j;" L_i is the systematic error due to laboratory "i," and ε_{ijk} is the random intralaboratory error.

Taking natural logarithms, it follows that

$$\ell n\, X_{ijk} = \ell n\, \beta_j + \gamma_j\, \ell n\, C_k + \ell n\, L_i + \ell n\, \varepsilon_{ijk} \qquad (2)$$

which is a linear regression model with dependent variable $\ell n\, X_{ijk}$ and independent variable $\ell n\, C_k$. (Details and justification for this model are discussed in the section "Comparison of Accuracy and Precision Across Water Types.")

The natural logarithms of the individual laboratory's data were regressed against the natural logarithms of the true concentration levels for the six ampuls in each water type. The predicted values for $\ell n \hat{X}_{ijk}$ were obtained from the regression equation, and the missing values for X_{ijk} were estimated by $\hat{X}_{ijk} = \exp(\ell n \hat{X}_{ijk})$. (For complete details of this procedure, see Reference 2.)

An example of the use of Youden's laboratory ranking procedure is presented in Table 5, where the rankings of the values for 4-chlorophenyl phenyl ether in water 3 are listed for each laboratory and for ampuls 1 through 6. For 20 laboratories and 6 ampuls, the upper and lower critical limits of the sums of the rankings are 104 and 22. If the sum of the rankings of any laboratory equals or exceeds 104, or is equal to or less than 22, that laboratory's data are rejected for all determinations for that analyte (4-chlorophenyl phenyl ether) in that water (water 3). From Table 5 it is apparent that the data from laboratories 2, 11, and 13 must be rejected. The estimated missing data were then removed from the data sets.

Test for Individual Outliers

The data remaining after rejection of zero, missing, "less than," and "nondetect" data were subjected to an individual outlier test based on calculation of the average value, $\bar{X}$, for each ampul and the standard deviation of the remaining values.

TABLE 5. YOUDEN LABORATORY RANKING PROCEDURE FOR 4-CHLOROPHENYL PHENYL ETHER IN WATER 3

Laboratory number	Ranking values						Cumulative score
	Ampul 1	Ampul 2	Ampul 3	Ampul 4	Ampul 5	Ampul 6	
1	9	9	14	11	9.5	10	62.5
2	4	1	1	2	5	3	16[a]
3	13	10	10	7	13	12	65
4	3	3	11	4	9.5	4	34.5
5	10	14	12	10	11	14	71
6	15	19	15	18	17	8	92
7	19.5	17	2	1	19.5	1	60
8	19.5	8	9	12	19.5	13	81
9	11	4	4	8	8	5	40
10	14	11	18	17	16	6	82
11	17	20	19	15	18	17	106[a]
12	18	18	13	13	12	20	94
13	2	2	3	3	2	2	14[a]
14	5	6	5	6	7	9	38
15	8	15	16.5	19	4	18	80.5
16	7	5	6	9	6	7	40
17	1	16	8	14	1	15	55
18	6	7	7	5	3	11	39
19	12	13	20	20	14	19	98
20	16	12	16.5	16	15	16	91.5

[a]Laboratories rejected versus upper and lower criteria of 104 and 22.

The criterion for rejection of individual outliers is based on calculation of Thompson's T-value [3,6].

In these calculations the mean recovery, $\bar{X}$, is given by

$$\bar{X} = \frac{1}{n} \sum_{i=1}^{n} X_i \qquad (3)$$

and the standard deviation, s, is given by

$$s = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2} \qquad (4)$$

where X_i = individual analyses
n = number of retained analyses values in the ampul set

The Thompson's T-test is defined as

$$T_i = \frac{X_e - \bar{x}}{s} \qquad (5)$$

where X_e is the retained X_i value farthest away from the mean ($\bar{X}$) of the set of retained data. The data point may be rejected if the value of T calculated exceeds critical values for T (two-sided test 5% significance level) as presented in Table 6. If the extreme value is rejected as an outlier, the test is repeated for the next most extreme value among the remaining data until the value being tested passes the test.

Table 7 summarizes calculations to examine suspect data points for 4-chlorophenyl phenyl ether in water 3 by the T-test for outliers. Four additional data points are identified as outliers. Of the original 120 data points for 4-chlorophenyl phenyl ether in water 3 (20 laboratories x 6 ampuls), all data points for laboratories 2, 11, and 13 were rejected on the basis of Youden's laboratory ranking procedure (total of 18 points), and four additional data points were found to be outliers based on Thompson's T-test (for a total of the 22 data points). These same outlier tests were applied for all five analytes in the six water matrices. All outlier data points are marked with an asterisk in Appendix B.

STATISTICAL SUMMARIES

After the outlier rejection tests were performed, the following summary statistics were calculated employing the remaining data for each ampul (single analyte, single concentration, single water matrix):

TABLE 6. CRITICAL VALUES FOR THOMPSON'S T (TWO-SIDED TEST) WHEN STANDARD DEVIATION IS CALCULATED FROM THE SAME SAMPLES

Number of observations, n	5% significance level
3	1.15
4	1.48
5	1.71
6	1.89
7	2.02
8	2.13
9	2.21
10	2.29
11	2.36
12	2.41
13	2.46
14	2.51
15	2.55
16	2.58
17	2.62
18	2.65
19	2.68
20	2.71

TABLE 7. RESULTS OF TESTS FOR INDIVIDUAL OUTLIERS (4-CHLOROPHENYL PHENYL ETHER IN WATER 3)

Ampul	Laboratory	Extreme value x_e	Mean $\bar{x}$	Standard deviation s	Calculated T $\frac{x_e - \bar{x}}{s} = T$	Number of points n	Critical T T_c	Decision
1	17	40.05	11.64	8.97	3.17	15	2.55	Reject
4	7	813.40	319.03	170.02	2.91	17	2.62	Reject
5	17	34.05	7.73	7.67	3.43	15	2.55	Reject
6	7	213.40	88.83	46.70	2.67	17	2.62	Reject

- Number of retained data points, n
- Mean recovery of retained data, $\bar{X}$
- Accuracy as a percent of relative error, % RE
- Overall absolute standard deviation, S
- Percent relative overall standard deviation, % RSD
- Absolute single-analyst standard deviation, SR
- Percent relative single-analyst standard deviation, % RSD-SA

All of these statistics, except the single-analyst absolute and relative standard deviations, were calculated using the retained data for each ampul. The basic statistical formulas used for these calculations are given below, where X_1, X_2,..., X_n denote the values for the n retained data points for a given ampul.

Mean Recovery ($\bar{X}$):

$$\bar{X} = \frac{1}{n} \sum_{i=1}^{n} X_i \qquad (3)$$

Accuracy as a % Relative Error:

$$\% \text{ RE} = \frac{\bar{X} - \text{true value}}{\text{true value}} \times 100 \qquad (6)$$

Overall Standard Deviation:

$$S = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (X_i - \bar{X})^2} \qquad (4)$$

and

Percent Relative Overall Standard Deviation:

$$\% \text{ RSD} = \frac{S}{\bar{X}} \times 100 \qquad (7)$$

The overall standard deviation, S, indicates the precision associated with measurements generated by a group of laboratories. This represents the broad variation in the data collected in a collaborative study. A measure of how well an individual analyst can expect to perform in his own laboratory is another important measure of precision. This single-analyst precision, denoted by SR, is measured by

$$SR = \sqrt{\frac{1}{2(m-1)} \sum_{i=1}^{m} (D_i - \bar{D})^2} \qquad (8)$$

where m = number of retained Youden-paired observations
D_i = difference between observations in the i^{th} pair
$\bar{D}$ = average of D_i values

The Youden-pair design employed in this study permits the calculation of single-analyst precision without duplicate measurements on the same sample and helps to avoid the well-intentioned manipulation of data that can occur when laboratories make duplicate analyses.

The percent relative standard deviation for the single-analyst precision is calculated by

$$\% \text{ RSD-SA} = \frac{SR}{\bar{X}^*} \times 100 \qquad (9)$$

where $\bar{X}^*$ is the average of the two mean recoveries corresponding to the two ampuls defining the particular Youden pair. These summary statistics are presented in Tables 8 through 12 for each of the five haloether compounds in the six water matrices.

TABLE 8. STATISTICAL SUMMARY FOR *BIS*(2-CHLOROISOPROPYL)-ETHER ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	1	5	1	5	1	5	1	5	1	5	1	5
NUMBER OF DATA POINTS	13	15	14	11	16	15	15	14	7	9	16	17
TRUE CONC (C) UG/L	3.00	2.40	3.00	2.40	3.00	2.40	3.00	2.40	3.00	2.40	3.00	2.40
MEAN RECOVERY (X)	4.01	3.83	3.18	2.97	3.10	2.04	4.03	3.87	2.84	4.47	2.64	2.41
ACCURACY(%REL ERROR)	33.62	59.72	6.05	23.83	3.37	-14.92	34.31	61.34	-5.19	86.30	-11.96	0.51
OVERALL STD DEV (S)	2.24	2.15	1.90	1.43	2.17	0.97	3.65	3.41	1.97	4.53	1.33	1.45
OVERALL REL STD DEV, %	56.00	55.97	59.71	48.20	69.93	47.28	90.66	88.00	69.36	101.21	50.39	60.06
SINGLE STD DEV, (SR)	1.83		0.49		1.51		1.09		1.16		0.93	
ANALYST REL DEV, %	46.55		15.94		58.74		27.63		31.82		36.61	
MEDIUM YOUDEN PAIR	2	6	2	6	2	6	2	6	2	6	2	6
NUMBER OF DATA POINTS	18	18	18	17	20	20	19	19	19	18	19	20
TRUE CONC (C) UG/L	132.00	92.00	132.00	92.00	132.00	92.00	132.00	92.00	132.00	92.00	132.00	92.00
MEAN RECOVERY (X)	107.94	82.75	100.77	69.13	91.41	76.11	98.47	69.46	112.69	80.46	103.99	74.94
ACCURACY(%REL ERROR)	-18.23	-10.05	-23.66	-24.86	-30.75	-17.27	-25.40	-24.50	-14.63	-12.54	-21.22	-18.54
OVERALL STD DEV (S)	47.49	26.05	38.13	22.08	37.94	39.43	42.36	26.17	53.69	43.20	50.63	34.50
OVERALL REL STD DEV, %	43.99	31.48	37.84	31.94	41.51	51.80	43.02	37.67	47.64	53.70	48.69	46.04
SINGLE STD DEV, (SR)	18.48		15.19		31.63		17.78		31.21		29.49	
ANALYST REL DEV, %	19.39		17.88		37.77		21.18		32.32		32.96	
HIGH YOUDEN PAIR	3	4	3	4	3	4	3	4	3	4	3	4
NUMBER OF DATA POINTS	19	18	19	18	20	19	20	20	20	19	19	19
TRUE CONC (C) UG/L	486.00	624.00	486.00	624.00	486.00	624.00	486.00	624.00	486.00	624.00	486.00	624.00
MEAN RECOVERY (X)	448.24	501.08	394.51	520.16	381.44	477.27	353.76	476.86	463.92	464.09	380.90	527.38
ACCURACY(%REL ERROR)	-7.77	-19.70	-18.82	-16.64	-21.51	-23.51	-27.21	-23.58	-4.54	-25.63	-21.63	-15.48
OVERALL STD DEV (S)	165.25	165.92	158.27	176.94	181.35	194.58	163.45	190.36	265.40	185.78	144.41	199.61
OVERALL REL STD DEV, %	36.87	33.11	40.12	34.02	47.54	40.77	46.20	39.92	57.21	40.03	37.91	37.85
SINGLE STD DEV, (SR)	102.39		56.35		93.91		110.30		123.28		106.50	
ANALYST REL DEV, %	21.57		12.32		21.87		26.56		26.57		23.45	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE 9. STATISTICAL SUMMARY FOR *BIS*(2-CHLOROETHYL)ETHER ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	1	5	1	5	1	5	1	5	1	5	1	5
NUMBER OF DATA POINTS	12	15	12	13	16	14	14	13	13	12	16	15
TRUE CONC (C) UG/L	1.40	1.60	1.40	1.60	1.40	1.60	1.40	1.60	1.40	1.60	1.40	1.60
MEAN RECOVERY (X)	1.24	2.40	1.61	1.47	1.48	1.28	1.24	1.32	8.98	8.67	1.24	1.19
ACCURACY(%REL ERROR)	-11.73	50.29	15.12	-8.32	5.80	-20.27	-11.48	-17.64	541.21	442.08	-11.47	-25.58
OVERALL STD DEV (S)	0.54	2.19	0.76	0.83	1.18	0.48	0.57	0.60	7.84	6.62	0.74	0.39
OVERALL REL STD DEV, %	43.93	90.88	46.95	56.89	79.77	37.39	45.91	45.21	87.31	76.37	59.53	32.80
SINGLE STD DEV, (SR)	0.64		0.53		0.32		0.40		3.60		0.32	
ANALYST REL DEV, %	35.00		34.53		22.89		31.34		40.76		26.74	
MEDIUM YOUDEN PAIR	2	6	2	6	2	6	2	6	2	6	2	6
NUMBER OF DATA POINTS	17	16	18	18	20	19	17	16	18	17	18	19
TRUE CONC (C) UG/L	108.00	87.00	108.00	87.00	108.00	87.00	108.00	87.00	108.00	87.00	108.00	87.00
MEAN RECOVERY (X)	79.40	73.70	76.64	63.83	70.90	55.52	70.04	57.24	90.25	69.03	76.46	58.13
ACCURACY(%REL ERROR)	-26.48	-15.29	-29.04	-26.63	-34.35	-36.19	-35.15	-34.21	-16.43	-20.66	-29.20	-33.19
OVERALL STD DEV (S)	33.50	10.96	32.95	24.52	32.20	25.99	30.39	20.37	36.21	23.65	31.07	20.89
OVERALL REL STD DEV, %	42.20	14.87	42.99	38.42	45.41	46.82	43.39	35.58	40.12	34.27	40.64	35.93
SINGLE STD DEV, (SR)	15.45		14.19		16.45		13.22		11.73		15.41	
ANALYST REL DEV, %	20.19		20.20		26.02		20.77		14.73		22.90	
HIGH YOUDEN PAIR	3	4	3	4	3	4	3	4	3	4	3	4
NUMBER OF DATA POINTS	18	17	18	18	20	20	18	18	18	17	19	19
TRUE CONC (C) UG/L	602.00	402.00	602.00	402.00	602.00	402.00	602.00	402.00	602.00	402.00	602.00	402.00
MEAN RECOVERY (X)	490.23	321.82	416.22	302.87	407.85	297.82	409.67	307.51	438.52	298.20	426.51	327.25
ACCURACY(%REL ERROR)	-18.57	-19.94	-30.86	-24.66	-32.25	-25.92	-31.95	-23.51	-27.16	-25.82	-29.15	-18.60
OVERALL STD DEV (S)	163.56	99.74	179.45	115.08	219.25	151.45	202.21	108.56	181.73	104.51	186.83	142.60
OVERALL REL STD DEV, %	33.36	30.99	43.11	38.00	53.76	50.85	49.36	35.30	41.44	35.05	43.80	43.57
SINGLE STD DEV, (SR)	77.42		58.61		97.90		110.51		66.82		90.97	
ANALYST REL DEV, %	19.07		16.30		27.75		30.82		18.14		24.14	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE 10. STATISTICAL SUMMARY FOR *BIS*(2-CHLOROETHOXY)METHANE BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	1	5	1	5	1	5	1	5	1	5	1	5
NUMBER OF DATA POINTS	10	10	11	13	13	14	16	12	11	12	15	14
TRUE CONC (C) UG/L	1.40	1.00	1.40	1.00	1.40	1.00	1.40	1.00	1.40	1.00	1.40	1.00
MEAN RECOVERY (X)	1.05	0.87	1.26	1.54	1.09	1.59	2.44	0.99	3.25	3.07	1.77	1.71
ACCURACY(%REL ERROR)	-24.71	-12.80	-9.68	54.00	-22.47	59.36	74.20	-0.92	132.27	206.83	26.10	71.07
OVERALL STD DEV (S)	0.54	0.33	0.76	1.89	0.63	2.22	3.29	0.76	3.29	3.06	1.02	1.63
OVERALL REL STD DEV, %	51.35	38.12	60.38	122.87	57.85	139.48	134.79	76.63	101.21	99.66	57.59	95.04
SINGLE STD DEV, (SR)	0.35		0.51		0.31		0.83		2.07		0.64	
ANALYST REL DEV, %	36.26		36.07		23.11		48.36		65.65		36.67	
MEDIUM YOUDEN PAIR	2	6	2	6	2	6	2	6	2	6	2	6
NUMBER OF DATA POINTS	15	17	18	18	19	19	17	16	18	17	18	19
TRUE CONC (C) UG/L	106.00	126.00	106.00	126.00	106.00	126.00	106.00	126.00	106.00	126.00	106.00	126.00
MEAN RECOVERY (X)	76.40	88.96	70.23	90.00	61.38	79.80	69.25	77.97	74.98	97.56	71.75	85.63
ACCURACY(%REL ERROR)	-27.92	-29.40	-33.75	-28.57	-42.09	-36.67	-34.67	-38.12	-29.27	-22.57	-32.31	-32.04
OVERALL STD DEV (S)	21.93	24.91	25.89	28.85	26.22	42.94	17.79	29.57	24.64	25.73	24.30	27.30
OVERALL REL STD DEV, %	28.71	28.00	36.87	32.05	42.71	53.81	25.69	37.92	32.86	26.38	33.86	31.89
SINGLE STD DEV, (SR)	17.74		23.21		25.90		16.64		19.03		19.42	
ANALYST REL DEV, %	21.45		28.97		36.70		22.61		22.06		24.68	
HIGH YOUDEN PAIR	3	4	3	4	3	4	3	4	3	4	3	4
NUMBER OF DATA POINTS	17	16	18	17	19	19	18	18	19	19	19	19
TRUE CONC (C) UG/L	398.00	528.00	398.00	528.00	398.00	528.00	398.00	528.00	398.00	528.00	398.00	528.00
MEAN RECOVERY (X)	294.18	360.72	270.47	374.52	254.29	359.95	253.53	378.58	268.32	391.46	251.82	391.97
ACCURACY(%REL ERROR)	-26.08	-31.68	-32.04	-29.07	-36.11	-31.83	-36.30	-28.30	-32.58	-25.86	-36.73	-25.76
OVERALL STD DEV (S)	95.51	143.96	114.56	134.69	127.81	174.93	120.98	158.43	99.92	171.44	104.77	161.40
OVERALL REL STD DEV, %	32.47	39.91	42.36	35.96	50.26	48.60	47.72	41.85	37.24	43.80	41.61	41.18
SINGLE STD DEV, (SR)	62.92		46.10		65.75		78.91		81.02		89.36	
ANALYST REL DEV, %	19.21		14.29		21.41		24.97		24.56		27.76	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE 11. STATISTICAL SUMMARY FOR 4-CHLOROPHENYL PHENYL ETHER ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	1	5	1	5	1	5	1	5	1	5	1	5
NUMBER OF DATA POINTS	12	13	14	14	14	14	16	14	17	15	17	13
TRUE CONC (C) UG/L	14.50	6.60	14.50	6.60	14.50	6.60	14.50	6.60	14.50	6.60	14.50	6.60
MEAN RECOVERY (X)	12.91	7.53	10.81	5.74	9.61	5.85	8.99	5.47	21.14	25.56	9.59	6.46
ACCURACY(%REL ERROR)	-10.95	14.15	-25.46	-13.06	-33.73	-11.43	-38.00	-17.11	45.76	287.20	-33.85	-2.12
OVERALL STD DEV (S)	6.96	3.31	5.37	2.99	4.50	2.49	5.27	2.46	20.23	32.61	6.00	2.85
OVERALL REL STD DEV, %	53.89	43.89	49.69	52.19	46.85	42.55	58.57	44.92	95.70	127.60	62.57	44.17
SINGLE STD DEV, (SR)	3.94		2.60		2.52		2.58		19.67		3.08	
ANALYST REL DEV, %	38.53		31.47		32.56		35.63		84.24		38.37	
MEDIUM YOUDEN PAIR	2	6	2	6	2	6	2	6	2	6	2	6
NUMBER OF DATA POINTS	16	17	16	17	17	16	18	17	19	17	16	17
TRUE CONC (C) UG/L	94.00	120.00	94.00	120.00	94.00	120.00	94.00	120.00	94.00	120.00	94.00	120.00
MEAN RECOVERY (X)	77.55	105.75	69.83	94.42	66.37	81.05	70.79	79.61	79.21	84.58	69.42	80.44
ACCURACY(%REL ERROR)	-17.50	-11.87	-25.71	-21.32	-29.39	-32.46	-24.69	-33.66	-15.73	-29.52	-26.15	-32.97
OVERALL STD DEV (S)	36.33	30.25	19.33	31.43	20.95	35.03	29.56	29.63	29.93	33.05	22.36	30.98
OVERALL REL STD DEV, %	46.84	28.61	27.67	33.29	31.56	43.23	41.76	37.22	37.78	39.07	32.20	38.51
SINGLE STD DEV, (SR)	21.01		20.18		18.90		22.96		23.67		26.15	
ANALYST REL DEV, %	22.93		24.57		25.64		30.53		28.91		34.90	
HIGH YOUDEN PAIR	3	4	3	4	3	4	3	4	3	4	3	4
NUMBER OF DATA POINTS	17	16	17	17	17	16	18	18	19	19	17	17
TRUE CONC (C) UG/L	489.00	424.00	489.00	424.00	489.00	424.00	489.00	424.00	489.00	424.00	489.00	424.00
MEAN RECOVERY (X)	412.77	337.79	369.14	324.91	347.88	288.13	288.86	278.96	354.17	304.10	324.18	340.48
ACCURACY(%REL ERROR)	-15.59	-20.33	-24.51	-23.37	-28.86	-32.04	-40.93	-34.21	-27.57	-28.28	-33.71	-19.70
OVERALL STD DEV (S)	160.38	161.92	169.19	161.97	151.08	134.70	131.02	128.89	165.06	142.01	119.35	145.88
OVERALL REL STD DEV, %	38.85	47.94	45.83	49.85	43.43	46.75	45.36	46.20	46.60	46.70	36.82	42.84
SINGLE STD DEV, (SR)	60.08		42.25		63.61		60.64		77.01		75.37	
ANALYST REL DEV, %	16.01		12.17		20.00		21.36		23.40		22.68	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE 12. STATISTICAL SUMMARY FOR 4-BROMOPHENYL PHENYL ETHER ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	1	5	1	5	1	5	1	5	1	5	1	5
NUMBER OF DATA POINTS	13	13	13	13	17	17	17	16	15	13	17	15
TRUE CONC (C) UG/L	2.80	3.80	2.80	3.80	2.80	3.80	2.80	3.80	2.80	3.80	2.80	3.80
MEAN RECOVERY (X)	4.62	6.37	4.14	5.05	4.31	5.02	4.34	5.00	3.52	7.32	4.01	4.44
ACCURACY(%REL ERROR)	64.92	67.55	47.77	32.79	53.84	32.15	54.94	31.53	25.76	92.69	43.13	16.95
OVERALL STD DEV (S)	2.69	3.06	2.36	3.08	2.88	2.52	2.65	3.10	2.01	5.19	2.22	2.18
OVERALL REL STD DEV, %	58.21	48.10	57.05	61.04	66.78	50.20	61.08	62.10	57.14	70.88	55.41	49.15
SINGLE STD DEV, (SR)	1.56		1.31		1.83		1.71		2.83		1.42	
ANALYST REL DEV, %	28.45		28.63		39.14		36.69		52.21		33.67	
MEDIUM YOUDEN PAIR	2	6	2	6	2	6	2	6	2	6	2	6
NUMBER OF DATA POINTS	18	19	19	19	20	20	20	18	19	16	18	20
TRUE CONC (C) UG/L	145.00	116.00	145.00	116.00	145.00	116.00	145.00	116.00	145.00	116.00	145.00	116.00
MEAN RECOVERY (X)	127.27	100.21	120.92	92.58	117.09	93.80	128.84	92.73	139.29	88.26	119.29	96.82
ACCURACY(%REL ERROR)	-12.23	-13.61	-16.61	-20.19	-19.25	-19.14	-11.15	-20.06	-3.94	-23.91	-17.73	-16.53
OVERALL STD DEV (S)	68.12	47.27	58.63	45.06	55.47	48.56	64.10	44.37	72.24	35.82	56.46	50.02
OVERALL REL STD DEV, %	53.52	47.17	48.49	48.67	47.38	51.77	49.75	47.85	51.87	40.59	47.33	51.66
SINGLE STD DEV, (SR)	40.52		36.30		37.03		43.80		41.71		41.08	
ANALYST REL DEV, %	35.63		34.01		35.12		39.53		36.66		38.01	
HIGH YOUDEN PAIR	3	4	3	4	3	4	3	4	3	4	3	4
NUMBER OF DATA POINTS	19	18	19	18	19	20	20	20	19	18	18	20
TRUE CONC (C) UG/L	552.00	626.00	552.00	626.00	552.00	626.00	552.00	626.00	552.00	626.00	552.00	626.00
MEAN RECOVERY (X)	487.29	493.91	455.45	532.26	425.42	489.42	408.19	426.32	436.61	400.71	365.32	553.24
ACCURACY(%REL ERROR)	-11.72	-21.10	-17.49	-14.97	-22.93	-21.82	-26.05	-31.90	-20.90	-35.99	-33.82	-11.62
OVERALL STD DEV (S)	206.47	233.38	213.11	245.99	194.26	261.97	189.98	213.89	263.81	173.96	162.07	256.45
OVERALL REL STD DEV, %	42.37	47.25	46.79	46.22	45.66	53.53	46.54	50.17	60.42	43.41	44.36	46.35
SINGLE STD DEV, (SR)	74.00		51.96		88.72		86.86		98.49		110.51	
ANALYST REL DEV, %	15.08		10.52		19.40		20.82		23.52		24.06	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

REGRESSION ANALYSIS OF BASIC STATISTICS

Systematic relationships frequently exist between the mean recovery statistics and the true concentration levels across ampuls, and between the precision statistics and the mean recovery statistics. Given a plot of precision values versus concentration levels, a smooth curve drawn through the points can show that the precision is found to (1) be constant and not vary with level; (2) vary directly with level in a linear manner; or (3) vary with level in a curvilinear fashion.

In order to derive statements for method accuracy and precision, the basic statistics were regressed assuming linear relationships, fitting the data to a line using weighted least-squares. The weights were chosen to be inversely related to the true concentration in the case of accuracy and inversely related to the mean recovery in the case of precision. The inverse weightings were employed to moderate the influence of the high Youden-pair data. The results of the regression analyses are discussed below.

Statements of Method Accuracy

The accuracy of Method 611 is characterized by comparing the mean recovery of the analyte, $\bar{X}$, to the true concentration level of the compound, C, in the water sample. In order to obtain a mathematical expression for this relationship, a regression line of the form

$$X = aC + b \qquad (10)$$

was fitted to the data by regression techniques.

The true concentration values often vary over a wide range. In such cases, the mean recovery statistics associated with the larger concentration values tend to dominate the fitted regression line

producing relatively larger errors in the estimates of mean recovery at the lower concentration values. In order to eliminate this problem, a weighted least squares technique was used to fit the mean recovery data to the true concentration values. The weighted least squares technique was performed by dividing both sides of Equation (10) by C resulting in Equation (11)

$$\frac{\bar{X}}{C} = a + b\left(\frac{1}{C}\right) \qquad (11)$$

which can then be converted to the desired relationships by multiplying through by C, giving:

$$\bar{X} = aC + b \qquad (12)$$

These equations were presented earlier in Table 1.

If the intercept "b" associated with the fitted line is negligible (i.e., essentially zero), then the slope "a" provides a unique value which represents the percent recovery over all of the concentration levels.

Statements of Method Precision

The precision of Method 611 is characterized by comparing the overall and single-analyst standard deviations to the mean recovery, $\bar{X}$. The IMVS program conducts these calculations via matrix algebra, where a weighted least-squares linear regression of S and SR versus $\bar{X}$ is conducted with weights chosen to be inversely proportional to the square of the mean recovery (see page 108 of Reference 2 for details). This method is equivalent to that suggested by Britton [7] where the linear regressions for

S and SR versus C are achieved by using the customary least-squares procedure to fit the equation:

$$\frac{S}{C} = c + d \frac{1}{C} \qquad (13)$$

In this study, however, the regression was conducted versus $\bar{X}$ as follows:

$$\frac{S}{\bar{X}} = c + d \frac{1}{\bar{X}} \qquad (14)$$

which is then converted by multiplying through by $\bar{X}$ to yield the linear relationships

$$S = a\bar{X} + b \qquad (15)$$

and

$$SR = c\bar{X} + d \qquad (16)$$

These equations also were presented earlier in Tables 1 and 2.

If the intercepts, b and d, are negligible, then the slopes, a and c, are good approximations of the overall and single-analyst percent relative standard deviations, respectively. These, in turn, are measures of the method precision.

COMPARISON OF ACCURACY AND PRECISION ACROSS WATER TYPES

It is possible that the accuracy and precision of Method 611 depend on the water type analyzed. The summary statistics $\bar{X}$, S, and SR are calculated separately for each concentration level within each water type. They can be compared across water types in order to obtain information about the effects of water type on

accuracy and precision. However, the use of these summary statistics in this manner has several disadvantages. First, it is cumbersome because there are 36 mean recovery statistics ($\bar{X}$) (six ampuls x six waters), 36 overall precision statistics (S), and 18 single-analyst precision statistics (SR) calculated for each compound. Comparison of these statistics across concentration levels and across water types becomes unwieldy. Second, the statistical properties of this type of comparison procedure are difficult to determine. Finally, due to variation associated with $\bar{X}$, S, and SR, comparisons based on these statistics can lead to inconsistent conclusions about the effect of water type. For example, distilled water may appear to produce a significantly lower value than drinking water for the precision statistic S at a high concentration, but a significantly higher value for S at a low concentration.

An alternative approach [2], has been developed to test for the effects of water type. This alternative approach is based on the concept of summarizing the average effect of water type across concentration levels rather than studying the local effects at each concentration level. If significant differences are established by this alternative technique, then the summary statistics can be used for further local analysis.

The test for the effect of water type is calculated using the following statistical model. If X_{ijk} denotes the measurement reported by laboratory "i," for water type "j," and ampul "k," then

$$X_{ijk} = \beta_j \cdot C_k^{\gamma_j} \cdot L_i \cdot \varepsilon_{ijk} \qquad (1)$$

where $i = 1,2,\ldots, n$
$j = 1,2,\ldots, 6$
$k = 1,2,\ldots, 6$

Model components β_j and γ_j are fixed parameters that determine the effect of water type j on the behavior of the observed measurements (X_{ijk}). The parameter C_k is the true concentration level associated with ampul "k." The model component L_i is a random factor which accounts for the systematic error associated with laboratory "i." The model component ε_{ijk} is the random factor that accounts for the intralaboratory error.

The model is designed to approximate the global behavior of the data. The multiplicative structure was chosen because of two important properties. First, it allows for a possible curvilinear relationship between the data (X_{ijk}) and the true concentration level (C_k) through the use of the exponent γ_j on C_k. This makes the model more flexible in comparison to straight-line models. Second, as will be noted below, an inherent increasing relationship exists between the variability in the data and the concentration level C_k in this model. This property is important because it is typical of interlaboratory data collected under conditions where the true concentration levels vary widely.

Accuracy is related directly to the mean recovery or expected value of the measurements (X_{ijk}). The expected value for the data modeled by Equation 1 is

$$E(X_{ijk}) = \beta_j \cdot C_k^{\gamma_j} \cdot E(L_i \cdot \varepsilon_{ijk}) \qquad (17)$$

Precision is related to the variability in the measurements (X_{ijk}). The variance of the data modeled by Equation 1 is

$$Var(X_{ijk}) = \left[\beta_j \cdot C_k^{\gamma_j}\right]^2 Var(L_i \cdot \varepsilon_{ijk}), \qquad (18)$$

which is an increasing function of C_k. (See Reference 2 for a complete discussion of this model.)

The accuracy and precision of Method 611 depend upon water type through Equations 17 and 18 and the parameters β_j and γ_j. If β_j and γ_j vary with j (i.e., vary across water type), then the accuracy and precision of the method also vary across water type.

To determine if these parameters do vary across water type and to compare their values, they must be estimated from the laboratory data using regression techniques. Equation 1 represents the basic model. However, taking natural logarithms of both sides of Equation 1, the following straight line regression model is obtained.

$$\ell n\, X_{ijk} = \ell n\, \beta_j + \gamma_j\, \ell n\, C_k + \ell n\, L_i + \ell n\, \varepsilon_{ijk} \qquad (2)$$

The parameter $\ell n\, \beta_j$ is the intercept, and γ_j is the slope of the regression line associated with water type "j." It is assumed that $\ell n\, L_i$ is normally distributed with mean 0 and variance σ_L^2, that $\ell n\, \varepsilon_{ijk}$ is normally distributed with mean 0 and variance σ_ε^2, and that the $\ell n\, L_i$ and $\ell n\, \varepsilon_{ijk}$ terms are independent.

Based on Equation 2, the comparison of water types reduces to the comparison of straight lines. Distilled water is viewed as a control, and each of the remaining lines is compared directly to the line for distilled water.

Using the data on the log-log scale and regression techniques, the parameter $\ell n\, \beta_j$ (and hence β_j) and γ_j can be estimated. These estimates are then used to test the null hypothesis that there is no effect due to water type. The formal null and alternative hypothesis, H_0 and H_A, respectively are given by:

$$H_0: \quad \ell n\, \beta_j - \ell n\, \beta_1 = 0 \text{ and } \gamma_j - \gamma_1 = 0 \text{ for } j = 2 \qquad (19)$$

$$H_A: \quad \ell n\, \beta_j - \ell n\, \beta_1 \neq 0 \text{ and/or } \gamma_j - \gamma_1 \neq 0 \text{ for some } j = 2 \qquad (20)$$

The null hypothesis (H_0) is tested against the alternative hypothesis (H_A) using an F-statistic. The probability of obtaining the value of an F-statistic as large as the value which was actually observed, Prob(F > F OBS), is calculated under the assumption that H_0 is true. H_0 is rejected in favor of H_A if Prob(F > F OBS) is less than 0.05.

If H_0 is not rejected, then there is no evidence in the data that the β_j vary with "j" or that the γ_j vary with "j." Therefore, there is no evidence of an effect due to water type on the accuracy or precision of the method. If H_0 is rejected, then some linear combination of the differences ($\ell n\ \beta_j - \ell n\ \beta$) and ($\gamma_j - \gamma_1$) is statistically different from zero. However, this does not guarantee there will be a statistically significant direct effect attributable to any specific water type since the overall F test can be overly sensitive to minor systematic effects common to several water types. The effect due to water type is judged to be statistically significant only if one of the differences, ($\ell n\ \beta_j - \ell n\ \beta_1$) and/or ($\gamma_j - \gamma_1$), is statistically different from zero. This is determined by checking the simultaneous 95% confidence intervals which are constructed for each of these differences. Each true difference can be stated to lie within its respective confidence interval with 95% confidence. If zero is contained within the confidence interval, then there is no evidence that the corresponding difference is significantly different from zero.

If at least one of the confidence intervals for the differences ($\ell n\ \beta_j - \ell n\ \beta_1$) or ($\gamma_j - \gamma_1$) fails to include zero, then the statistical significance of the effect due to water type has been established. However, establishment of a statistically significant effect due to water type does not necessarily mean that the effect is of practical importance. Practical importance is related to the size and interpretation of the differences.

The interpretation of the differences involves comparing the mean recovery and standard deviation for each water type to the mean recovery and standard deviation obtained for distilled water. These comparisons are made on a relative basis. The mean recovery for water type "j," given by Equation 17, is compared to that for distilled water (j = 1) on a relative basis by

$$\frac{E(X_{ijk})}{E(X_{ilk})} = \frac{\beta_j \, C_k^{\gamma_j} \, E(L_i \cdot \varepsilon_{ijk})}{\beta_1 \, C_k^{\gamma_1} \, E(L_i \cdot \varepsilon_{ilk})} = \frac{\beta_j}{\beta_1} C_k^{(\gamma_j - \gamma_1)} \qquad (21)$$

(The ratio of the standard deviations would be equivalent to Equation 21; therefore, the interpretation of the effect on precision is the same as that for the effect on mean recovery.)

The ratio in Equation 21 is a measure of the relative difference in mean recovery between water type "j" and distilled water. It is composed of two parts (a) β_j/β_1, which is independent of the true concentration level (i.e., the constant bias), and (b) $C_k^{(\gamma_j - \gamma_1)}$, which depends on the true concentration level (i.e., the concentration dependent bias). If $(\gamma_j - \gamma_1)$ is zero, then the relative difference in mean recovery is β_j/β_1, which is independent of concentration level C_k. Then the mean recovery of water type "j" is β_j/β_1 x 100 percent of the mean recovery for distilled water. If $(\gamma_j - \gamma_1)$ is not zero, then the mean recovery of water type "j" is $([\beta_j/\beta_1] \cdot C_k^{[\gamma_j - \gamma_1]})$ x 100% of that for distilled water, and therefore depends on the true concentration level C_k.

To illustrate these points, consider the following example. Suppose that a significant F-value has been obtained, and the confidence intervals for all of the differences contain zero except for water type 5. For water type 5, the point estimate for $(\ell n\ \beta_5 - \ell n\ \beta_1)$ is -0.38, and the confidence interval for $(\ell n\ \beta_5 - \ell n\ \beta_1)$ is (-0.69, -0.07). The point estimate for $(\gamma_5 - \gamma_1)$ is -0.07, and the

confidence interval for $(\gamma_5 - \gamma_1)$ is (-0.04, 0.18). In this case, a statistically significant effect due to water type has been established that involves only water type 5. The practical significance of this effect is judged by considering Equation 21. The ratio of mean recoveries for water type 5 and distilled water is given by

$$\frac{E(X_{i5k})}{E(K_{ilk})} = \frac{\beta_5}{\beta_1} C_k^{(\gamma_5 - \gamma_1)} \tag{22}$$

and the ratio of the standard deviations is given by

$$\sqrt{\frac{Var(X_{ijk})}{Var(X_{ilk})}} = \frac{\beta_5}{\beta_1} C_k^{(\gamma_5 - \gamma_1)} \tag{23}$$

Because the confidence interval for $(\gamma_5 - \gamma_1)$ contains zero, this difference is assumed to be insignificant and is set to zero. Therefore, Equations 22 and 23 reduce to β_5/β_1. The point estimate for $(\ell n\ \beta_5 - \ell n\ \beta_1)$ was -0.38. Therefore, the point estimate for β_5/β_1 is 0.68, and the mean recovery for water type 5 is estimated to be 68% of the mean recovery for distilled water. Similarly, the standard deviation for the data for water type 5 is estimated to be 68% of the standard deviation for distilled water. Since the 95% confidence interval for $(\ell n\ \beta_5 - \ell n\ \beta_1)$ was (-0.69, -0.07), any value in the interval (0.50, 0.93) is a reasonable estimate for β_5/β_1, and the mean recovery (standard deviation) for water type 5 can be claimed to be from 50% to 93% of the mean recovery (standard deviation) for distilled water. The practical significance of the effect due to water type 5 would depend on the importance of a mean recovery (standard deviation) that is between 50% and 93% of the mean recovery (standard deviation) observed for distilled water.

The comparison of accuracy and precision across water types just discussed, is based on the assumption that Equation (1) approximately models the data. It is clear that in practical monitoring programs of this type, such models cannot model the data completely in every case. This analysis, therefore, is viewed as a screening procedure which identifies those cases where differences in water types are likely to be present. A more detailed, local analysis can then be pursued using the basic summary statistics for precision and accuracy.

Results of the accuracy and precision comparison among the waters in the study are presented in Appendix C.

SECTION 6

RESULTS AND DISCUSSION

The objective of this study was to characterize the performance of Method 611 in terms of accuracy, overall precision, single-analyst precision, and the effect of water type on accuracy and precision.

One measure of the performance of the method is that 16.3% of the 3600 analytical values were rejected as outliers. Of the 16.3% outliers, 6.1% were rejected through application of Youden's laboratory ranking procedure and 10.2% were rejected employing the Thompson T-test.

ACCURACY

The accuracy of Method 611 is obtained by comparing the mean recovery, $\bar{x}$, to the true values of concentration in µg/L. In Tables 8 through 12, individual values of accuracy as percent relative error are listed for each analyte, in each water matrix, and at each of the six concentration levels in that water matrix (three Youden pairs). This results in 180 separate values for accuracy. The linear regression of mean recovery, $\bar{x}$, versus true concentration level, c, provides values representing the percent recovery over all of the concentration levels. This reduces the separate values for accuracy to 30, one value for each of five analytes in each of six waters. Table 13 presents the percent recovery for each compound in water types as measured by the slopes of the linear equations for recovery presented earlier in Table 1. In Table 13, the linear regression slopes are compared to percent recoveries calculated from the average of the

TABLE 13. METHOD 611 ACCURACY (%)

Water	BCIPE				BCEE			
	Slope[a]	Mean Recovery by Youden Pair[b] Low	Medium	High	Slope[a]	Mean Recovery by Youden Pair[b] Low	Medium	High
Water 1	85	147	86	86	81	119	79	81
Water 2	78	115	76	82	72	103	72	72
Water 3	77	94	79	78	67	93	65	71
Water 4	73	148	75	75	69	86	65	72
Water 5	83	141	86	85	72	592	81	74
Water 6	80	94	80	81	72	82	69	76
Average all waters	79	123	80	81	72	179	72	74

(continued)

TABLE 13 (continued)

Water	BCEXM				CPPE			
	Slope[a]	Mean Recovery by Youden Pair[b] Low	Medium	High	Slope[a]	Mean Recovery by Youden Pair[b] Low	Medium	High
Water 1	71	81	71	71	82	101	85	82
Water 2	67	122	69	69	75	81	72	76
Water 3	60	118	62	66	67	77	69	70
Water 4	65	96	64	68	65	72	71	62
Water 5	71	270	74	71	56	267	77	72
Water 6	67	149	68	69	69	92	70	73
Average all waters	67	139	68	69	69	115	74	73

(continued)

TABLE 13 (continued)

Water	BPPE				Average All Analytes			
	Slope[a]	Mean Recovery by Youden Pair[b] Low	Medium	High	Slope[a]	Mean Recovery by Youden Pair[b] Low	Medium	High
Water 1	85	166	87	84	81	123	82	81
Water 2	72	140	82	84	73	112	74	77
Water 3	78	141	81	78	70	105	71	73
Water 4	77	143	84	76	70	109	72	71
Water 5	81	159	86	74	73	280	80	73
Water 6	79	130	83	77	73	109	74	75
Average all waters	79	147	84	79	73	140	76	75

[a]Percent accuracy from slope of regression equations (Table 1).

[b]Mean percent recovery for Youden pairs (Tables 8-12).

quotients $\bar{x}$:c (presented in Tables 8 through 12) for all three Youden pairs individually.

The validity of using the slope to estimate the percent recovery depends up on the negligible magnitude for the intercept of the linear regression equation. From Table 13, it is evident that the linear regression slope agrees extremely well with the average recoveries from the medium and high Youden pair concentrations. Examination of Table 13 reveals that recoveries of the analytes in the low Youden pair samples often exceeded 100%. This could be attributed to difficulty in correcting for background interferences in the blank analyses. This cause is suggested for the high recoveries of BCEE and 4-CPPE in wastewater 2 (eg 582% and 267%, respectively). In these cases the intercepts of the regressions equations for accuracy in wastewater 2 were 7.77 for BCEE and 20.40 for 4-CPPE. Both values cannot be viewed as being insignificant. Because of these large intercepts, new linear regression equations were calculated for these two analytes in wastewater 2, as presented earlier in Table 2.

Therefore, it is evident that the driving force in determining the veracity of the use of the regression equation slope as the percent recovery throughout the concentration range studied is the low Youden pair values. Based upon the excellent agreement between the linear regression equation slopes and the average recoveries for the higher Youden pair samples, the values presented in Table 13 and earlier in Tables 1 and 2 are considered to be representative of the accuracy of Method 611.

PRECISION

The overall and single-analyst precisions of Method 611 were determined as percent relative standard deviations for each analyte, water type, and concentration level. As presented in Tables 8 through 12, 180 individual values of overall percent

relative standard deviation and 90 individual values of single-analyst percent relative standard deviation result. The linear regression of standard deviation, s, versus mean recovery, $\bar{x}$, provides values of percent relative standard deviation over all the concentration ranges. This reduces the separate measures of precision to 30, one value for each of five analytes in each of six water-types. Tables 14 and 15 present the percent relative standard deviations as measured by the slopes of the linear regression equations presented earlier in Table 1 for the overall and the single-analyst precision, respectively. These values are compared to the averages of the percent relative standard deviations presented in Tables 8 through 12 for all three individual Youden pairs.

From Tables 14 and 15, it is evident that the % RSD and % RSD-SA precision values obtained from the slopes of the linear regression equations presented in Table 1 agree very closely with the average precision values for the middle and high Youden pairs presented in Tables 8 through 12. This agreement offers support to the precision value obtained via the linear regression process.

The poor precision (high % RSD and % RSD-SA) values demonstrated in the low Youden pair samples in Tables 8 through 12 are attributed to background interferences in the water matrices for the low concentration range of the haloethers (1.0 to 3.8 µg/L).

Two questionable precision values are evident on examination of Tables 14 and 15. The first is the value of 32% RSD for chlorophenyl phenyl ether in water 5. In this case, the average % RSD from the middle and high Youden pair is 43%. The second questionable value also occurs for chlorophenyl phenyl ether in water 5 where the linear regression slope gives a value of 15% RSD-SA compared to an average of 26% for the middle and high Youden pairs and an average of 26% for the middle and high Youden pairs and an average of 46% for all Youden pairs. These unusual values can be attributed to interences in the wastewater 2 matrix.

TABLE 14 METHOD 611 PRECISION (% RSD)

Water	BCIPE				BCEE			
	Slope[a]	Mean % RSD by Youden Pair[b]			Slope[a]	Mean % RSD by Youden Pair[b]		
		Low	Medium	High		Low	Medium	High
Water 1	36	56	38	35	35	67	29	32
Water 2	36	54	35	37	40	52	41	41
Water 3	47	59	47	44	50	59	46	52
Water 4	40	89	40	43	41	46	39	42
Water 5	52	85	51	49	35	82	37	38
Water 6	42	55	47	38	41	46	38	44
Average all waters	42	66	43	41	40	59	38	42

(continued)

TABLE 14 (continued)

Water	BCEXM				CPPE			
	Slope[a]	Mean % RSD by Youden Pair[b]			Slope[a]	Mean % RSD by Youden Pair[b]		
		Low	Medium	High		Low	Medium	High
Water 1	33	45	28	36	41	59	38	43
Water 2	38	92	34	39	39	51	30	48
Water 3	53	99	48	49	42	45	37	45
Water 4	38	106	32	45	43	52	39	46
Water 5	34	100	30	41	32	112	38	47
Water 6	36	76	33	41	38	53	35	40
Average all waters	39	86	34	42	39	62	36	45

(continued)

TABLE 14 (continued)

Water	BPPE				Average All Analytes			
	Slope[a]	Mean % RSD by Youden Pair[b] Low	Medium	High	Slope[a]	Mean % RSD by Youden Pair[b] Low	Medium	High
Water 1	47	53	50	45	38	56	37	38
Water 2	47	59	49	47	40	62	38	42
Water 3	49	58	50	50	48	64	46	48
Water 4	48	62	49	48	42	71	40	45
Water 5	51	64	46	52	41	89	40	45
Water 6	47	52	49	45	41	56	40	42
Average all waters	48	58	49	48	42	66	40	44

[a] % RSD from slope of regression equations (Table 1).

[b] Mean % RSD for individual Youden pairs (Tables 8-12).

TABLE 15. METHOD 611 PRECISION (% RSD-SA)

Water	BCIPE				BCEE			
	Slope[a]	Mean % RSD-SA by Youden Pair[b] Low	Medium	High	Slope[a]	Mean % RSD-SA by Youden Pair[b] Low	Medium	High
Water 1	20	47	19	22	19	35	20	19
Water 2	15	16	18	12	18	35	20	16
Water 3	29	59	38	22	27	23	26	28
Water 4	24	28	21	27	26	31	21	31
Water 5	29	32	32	27	15	41	15	18
Water 6	28	37	33	23	23	27	23	24
Average all waters	24	37	27	22	21	32	21	23

(continued)

TABLE 15 (continued)

Water	BCEXM				CPPE			
	Slope[a]	Mean % RSD-SA by Youden Pair[b] Low	Medium	High	Slope[a]	Mean % RSD-SA by Youden Pair[b] Low	Medium	High
Water 1	20	36	21	19	18	39	23	16
Water 2	21	36	29	14	17	31	25	12
Water 3	29	23	37	21	22	33	26	20
Water 4	24	48	23	25	25	36	31	21
Water 5	22	66	22	25	15	84	29	23
Water 6	26	37	25	28	28	38	35	23
Average all waters	24	39	26	22	21	44	28	19

(continued)

TABLE 15 (continued)

Water	BPPE				Average All Analytes			
	Slope[a]	Mean % RSD-SA by Youden Pair[b] Low	Medium	High	Slope[a]	Mean % RSD-SA by Youden Pair[b] Low	Medium	High
Water 1	25	28	36	15	29	37	24	18
Water 2	22	29	34	11	19	29	25	13
Water 3	27	39	35	19	27	35	32	22
Water 4	30	37	40	21	26	36	27	22
Water 5	29	52	37	24	22	55	27	23
Water 6	31	34	38	24	27	35	31	24
Average all waters	27	37	37	19	24	38	28	20

[a] % RSD-SA from slope of regression equations (Table 1).

[b] Mean % RSD-SA for individual Youden pairs (Tables 8-12).

EFFECTS OF WATER TYPES

The comparison of accuracy and precision across water types is summarized in Table 16, where the observed F values and the probability of exceeding the F values are entered for each of the seven analytes.

For every analyte except 4-bromophenyl phenyl ether, the F-test suggests a statistically significant effect due to water type (P[F>observed F]<0.05). The null hypothesis test indicates that a statistically significant effect has been established at the 95% confidence limit for the following analyte - water combinations: *bis*(2-chloroisopropyl)ether in waters 3 and 6; *bis*(2-chloroethoxy) methane in waters 5 and 6; and 4-chlorophenyl phenyl ether in water 5. These effects are indicated since zero is not contained within the confidence limits for $(\ell n\beta_j - \ell n\beta_1)$ and/or $(\gamma_j - \gamma_1)$ for the above analyte-water combinations.

After examination of several factors including final regression equations for all waters and the absolute values of the point estimates, the only instance in which a practical significance is evident is for 4-chlorophenyl phenyl ether in wastewater 2. This analyte-water combination coincides with that which exhibited the lowest accuracy (Tables 1 and 13) and the largest discrepancies in precision (% RSD and % RSD-SA) between the linear regression equation slopes and the averages of the precision values (see Tables 14 and 15).

RESPONSES TO QUESTIONNAIRE

One of the goals of this study was to conduct the interlaboratory study of the haloether method in a manner consistent with how it would eventually be used. A number of decisions were made both prior to the study and after the prestudy conference concerning

TABLE 16. SUMMARY OF THE TEST FOR DIFFERENCE ACROSS WATER TYPES

Compound	Observed F-value	P[F>observed F]	F test statistically significant at the 5% level?	Statistical significance established by the 95% confidence limit?	Waters	Practical significance established by the 95% confidence limit?	Waters
bis(2-Chloroisopropyl)ether	2.73	0.0027	Yes	Yes	3,6	No	-
bis(2-Chloroethyl)ether	20.42	0.0000	Yes	Yes	5	No	-
bis(2-Chloroethoxy)methane	6.08	0.0000	Yes	Yes	5,6	No	-
4-Chlorophenyl phenyl ether	4.87	0.0000	Yes	Yes	5	Yes	5
4-Bromophenyl phenyl ether	0.32	0.975	No	-	-	-	-

which variables would be controlled and which variables would be allowed to contributate to a wider distribution of results. The method requires the use of halide-specific detectors. The use of Hall, Coulson, and Dohrmann detectors was recommended. The EC detector used by one laboratory was not recommended due to a lack of specificity. Examination of the data from that laboratory showed no acceptable values for BCEXM, but all values for BCIPE and 4CPPE were acceptable. The values for BCEE in four of the six waters for BPPE in five of the waters were acceptable employing the EC detector. It was also decided not to supply the participating laboratories with standards or calibration solutions. Rigidly controlled, however, was the use of only one specified column packing material, although the labs were required to purchase it themselves from any supplier they desired.

The method, as published in the Federal Register, had a recommended temperature program. One compound (2-chloroethyl vinyl ether), was dropped from the study late in the method's development due to its high volatility, which led to low and variable recovery. The Federal Register temperature program was not optimized to take advantage of this change in compounds. Because of the wide diversity of gas chromatographs and detectors being used, the laboratories were allowed to optimize the temperature programming for their equipment.

Other operational parameters were also suggested as a results of MC studies, for example, hydrogen flow rate, furnace temperatures, electrolyte composition and flow rate, and so forth. However, they were not mandated and were not even applicable for some of the detectors being used. The individual labcratories were to start with the method conditions and optimize for their particular instrumentation. It was found after the method study that there were some other laboratory practices which differed from laboratory to laboratory which were not specified in the method. The most striking was the variety of means which were

used to eliminate emulsion problems. Almost every laboratory had a different method to solve this problem. Some of these methods may be analytically superior to others. It was felt, however, that any of this wide array of methods used would probably be acceptable. The more questionable approaches were "heat gun and glass wool" and "gentle extraction" but the labs using these methods did not report significantly different data compared to the other labs.

Responses to these questionnaries are presented in Table 17, ordered in detector groupings.

In general, any of the acceptable detectors were shown to be capable of generating high quality results. It was initially believed that the use of a Hall 700A detector would be a significant advantage. This was not proven to be the case since the data are fairly randomly distributed.

Some of the laboratories that participated in the method validation study reported interference problems. The exact causes for these variances have not been determined, but several possibilities exist. Sample preparation techniques (especially the Florisil cleanup) could cause varying amounts and numbers of interferences in the final concentrate. The many GC/detector parameters could cause varying peak separations. Finally, there is always the possibility of accidental introduction of external interfering contaminates.

In the cleanup step of Method 611, Florisil seems to be most effective in removing compounds that elute during the last 70% of a GC analysis. Therefore, BCEXM, CPPE, and BPPE are easy to quantify even at low concentrations. Florisil was less effective on early eluting compounds, thus causing some interferences with BCIPE and BCEE. However, even with these two haloethers, the concentration

TABLE 17. LABORATORY ANALYTICAL CONDITIONS (ORDERED IN DETECTOR GROUPINGS)

Laboratory code	Detector	Good data points[a]	Gas chromatograph	Temperature program, °C	Helium flow rate, mL/min	Hydrogen flow rate, mL/min	Furnace temperature, °C	Electrolyte composition	Electrolyte flow rate, mL/min
11	Hall 700	7	Varian 1400	60° - 2 min 8°/min to 210°	40		900	Ethanol	0.3
12	Hall 700	1	Beckman 55	100° - 4 min 15°/min to 230°	40	37	875	n-Propanol	0.4
6	Hall 700	6	H-P (auto) 5730	100° - 4 min 8°/min to 230°	30	30	875	75/25 Ethanol/H_2O	0.5
15	Hall 700	2	Perkin-Elmer	Standard[c]			900	Isopropyl water	0.5
2	Hall 700	21	Perkin-Elmer 900	75° - 4 min 12°/min to 200°	35		895	75/25 Ethanol/H_2O	0.5
13	Hall 700	21	H-P 5750	60° - 2 min 8°/min to 230°	40	60	880	75/25 Ethanol/H_2O	3.5
18	Hall 700	13	H-P 5840A	Standard	35	30	900	90/10 Ethanol/H_2O	0.4
1	Hall 700	18	Varian 3700	Standard	30	70	900	75/25 Ethanol/H_2O	0.5
10	Hall 700A	4	Tracor 560	60° - 4 min 16°/min to 230°	30	30	900	Propanol	1
4	Hall 700A	23	Tracor 560	Standard	40	50	800	n-Propanol	1.3
16	Hall 700A	16	Tracor 560	100° - 4 min 16°/min to 220°	40	60	875	n-Propanol	0.6
8	Hall 700A	2	Tracor 560	70° - 2 min 8°/min to 230°	20	50	900	95/5 Ethanol/H_2O	0.3
17	Hall 700A	5	Tracor 560	80° - 8°/min to 210°	25	20	820	Isopropyl	0.5
7	Hall 700A	9	Tracor 560	Standard	30	20	820	n-Propanol	4
14	Hall 310[b]	15	Tracor 222	100° - 4 min 16°/min to 200°	25	80	925	75/25 Ethanol/H_2O	1.5
19	Hall 310	4	Tracor MT-2	60° - 2 min 7.5/min to 180°	40	35	910	Water	0.3
3	Coulson	8	Tracor 222	Standard	40	58	860		
5	U.S. G-1000 Coulson	18	H-P (auto) 5710	Standard	40	40	820	Water	1
9	Bohrmann DE-20 Coulson	6	Perkin-Elmer 9000	Standard	30	O_2 50	800	70% Acetic acid in H_2O	0
20	Electron capture	1	H-P 5730A		40				

(continued)

TABLE 17 (continued)

Laboratory code	Technique for eliminating emulsion	Concentration problems	Water interferences by wastewater number	Nondetection					Other
				Interference peaks	Poor detector sensitivity	Loss of analyte on Florisil	Baseline noise	Initial concentration too low	
11	2% NaCl					x	x	x	
12	Continuous extraction		2	x		x			High boiler memory
6	Na_2SO_4		2, 3					x	
15	Centrifuge								
2	Glass wool separatory funnel			x	x			x	
13	Na_2SO_4		1, 2, 3	x				x	
18	Gentle extraction		2, 3	x		x	x		
1	Glass wool	Too slow at 65°C							no problems
10	Na_2SO_4	Took 30 min with insul	1, 2	x			x		
4	Separatory funnel		2	x					
16	Glass wool + Na_2SO_4		2	x					
8	Whipping with wire		2			x		x	
17			2						no problems
7	Heat gun Glass wool		1, 2			x	x		
14	Centrifuge		2	x	x			x	Bumping, add chips on solvent exchange
19	Na_2SO_4	Too slow		x	x	x	x	x	
3									
5	Glass wool		2 Tap	x					Bumping, add chips on solvent exchange
9	Stirring centrifuge		2, 3	x				x	
20	Glass wool	Longer at temperature	1		x				

(continued)

TABLE 17 (continued)

Laboratory code	Linear response	Calibration method	Cause of day-to-day detector sensitivity	Recommendations
11	No <10	External standard	Temperature variation in the transfer lines	
12	Yes			Slow program to 10°/min for resolution from interferences
6	Fair			
15				Hall - not good
2	Yes			Better Hall design. Try SEP-PAK[a]
13	Yes		Electrolyte flow	Alternate cleanup for low concentrations
18	Yes	Linear plot	Electrolyte composition	
1	Yes >1 ng/mL			
10	Yes	Single point ~ concentration	Resin bed	Additional cleanup method for special problems
4	Yes	Linear plot		
16	No, almost	Single point	Coating of Ni tube	
8	Yes	Linear plot		
17	No			
7	Yes	1-100 ng linear		More effective cleanup needed
14	No	$\ln y = B_1 (\ln x)^2 + B_2 \ln x + B_3$	Fluctuation electrolyte flow - transfer line condensation	Raise detection limits. Stop at 200°C. Check SP-2330 vs. 1,000
19	Yes			Use Florisil on standards for better analysis
3	No	$y = ax^b$		
5	Yes >10 ng			Better cleanup
9	No, but close	Single point		Eliminate Florisil. Use GC/MS
20	Yes			

NOTE: Blanks indicate no response given in questionnaire.

[a]The average results of the six water samples was determined for each laboratory for each compound in each spiking solution. This gives 30 averages for each laboratory (5 compounds x 6 spiking solutions). This column shows how many of those values from each laboratory were within 20% of the true value.

[b]Used 700A for 1 and 5.

[c]The "standard" program furnished to the laboratories was 100° for 4 minutes, 16° per minute to 230°, and hold at 230° for 4 minutes. This gives a faster analysis than the example published in the Federal Register on December 3, 1979.

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could usually be determined by either subtracting blank interference values or changing the GC program to effect better separation. For more details including chromatograms and specific interfering compounds see Appendix D where other MC findings concerning Method 611 are presented.

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6. Thompson, W. R., "On a Criterion for the Rejection of Observations and the Distribution of the Ratio of the Deviation to the Sample Standard Deviations", The Annals of Mathematical Statistics, AASTA 6 (1935), pp. 214-219.

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APPENDIX A

TEST METHOD - HALOETHERS-METHOD 611

United States
Environmental Protection
Agency

Environmental Monitoring and
Support Laboratory
Cincinnati OH 45268

Research and Development

EPA

Test Method

Haloethers — Method 611

1. Scope and Application

1.1 This method covers the determination of certain haloethers. The following parameters can be determined by this method.

Parameter	STORET No.	CAS No
Bis(2-chloroethyl) ether	34273	111-44-4
Bis(2-chloroethoxy) methane	34278	111-91-1
Bis(2-chloroisopropyl) ether	34283	108-60-1
4-Bromophenyl phenyl ether	34636	101-55-3
4-Chlorophenyl phenyl ether	34641	7005-72-3

1.2 This is a gas chromatographic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1. When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second GC column that can be used to confirm measurements made with the primary column. Method 625 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for all of the parameters listed above, using the extract from this method.

1.3 The method detection limit (MDL, defined in Section 14.1)[1] for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from that listed, depending upon the nature of interferences in the sample matrix.

1.4 The sample extraction and concentration steps in this method are essentially the same as in methods 606, 608, 609, and 612. Thus, a single sample may be extracted to measure the parameters included in the scope of each of these methods. When cleanup is required, the concentration levels must be high enough to permit selecting aliquots, as necessary, to apply appropriate cleanup procedures. The analyst is allowed the latitude, under Gas Chromatography (Section 12), to select chromatographic conditions appropriate for the simultaneous measurement of combinations of these parameters.

1.5 Any modification of this method, beyond those expressly permitted, shall be considered as major modifications subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of

gas chromatography and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately one-liter, is solvent extracted with methylene chloride using a separatory funnel. The methylene chloride extract is dried and exchanged to hexane during concentration to a volume of 10 mL or less. GC conditions are described which permit the separation and measurement of the compounds in the extract using a halide specific detector[2].

2.2 The method provides a Florisil column cleanup procedure to aid in the elimination of interferences that may be encountered.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.5.

3.1.1 Glassware must be scrupulously cleaned.[3] Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. This should be followed by detergent washing with hot water, and rinses with tap water and reagent water. It should then be drained dry, and heated in a muffle furnace at 400°C for 15 to 30 minutes. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. The cleanup procedures in Section 11 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Table 1.

3.3 Dichlorobenzenes are known to coelute with haloethers under some gas chromatographic conditions. If these materials are present together in a sample, it may be necessary to analyze the extract with two different column packings to completely resolve all of the compounds.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified[4-8] for the information of the analyst.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Grab sample bottle - Amber glass, one-liter or one-quart volume, fitted with screw caps lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The container must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional) - Must incorporate glass sample containers for the collection of a minimum of 250 mL. Sample containers must be kept refrigerated at 4°C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only).

5.2.1 Separatory funnel - 2000-mL, with Teflon stopcock.

5.2.2 Drying column - Chromatographic column 400 mm long x 19 mm ID, with coarse frit.

5.2.3 Chromatographic column - 400-mm long x 19 mm ID glass with coarse fritted plate on bottom and Teflon stopcock (Kontes K-420540-0224 or equivalent).

5.2.4 Concentrator tube, Kuderna-Danish - 10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.5 Evaporative flask, Kuderna-Danish - 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.6 Snyder column, Kuderna-Danish - Three-ball macro (Kontes K-503000-0121 or equivalent).

5.2.7 Vials - Amber glass, 10- to 15- mL capacity, with Teflon-lined screwcap.

5.3 Boiling chips - Approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.

5.4 Water bath - Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

5.5 Balance - Analytical, capable of accurately weighing 0.0001 g.

5.6 Gas chromatograph - An analytical system complete with temperature programmable gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

5.6.1 Column 1 - 1.8 m long x 2 mm ID pyrex glass, packed with Supelcoport, (100/120 mesh) coated

with 3% SP-1000 or equivalent. This column was used to develop the method performance statements in Section 14. Guidelines for the use of alternate column packings are provided in Section 12.1.

5.6.2 Column 2 - 1.8 m long x 2 mm ID pyrex glass, packed with Tenax-GC (60/80 mesh) or equivalent.

5.6.3 Detector - Halide specific electrolytic conductivity or microcoulometric. These detectors have proven effective in the analysis of wastewaters for the parameters listed in the scope of this method. The Hall conductivity detector was used to develop the method performance statements in Section 14. Guidelines for the use of alternate detectors are provided in Section 12.1. Although less selective, an electron capture detector is an acceptable alternative.

6. Reagents

6.1 Reagent water - Reagent water is defined as a water in which an interferent is not observed at the MDL of each parameter of interest.

6.2 Sodium thiosulfate - (ACS) Granular.

6.3 Acetone, methanol, methylene chloride, hexane, and petroleum ether (boiling range 30 to 60°C) - Pesticide quality or equivalent.

6.4 Sodium sulfate - (ACS) Granular, anhydrous. Purify by heating at 400°C for four hours in a shallow tray.

6.5 Florisil - PR Grade (60/100 mesh), purchase activated at 1250°F and store in the dark in glass container with glass stoppers or foil-lined screw caps. Before use, activate each batch overnight at 130°C in a foil-covered glass container.

6.6 Ethyl ether - Nanograde, redistilled in glass, if necessary.

6.6.1 Must be free of peroxides as indicated by EM Laboratories Quant test strips. (Available from Scientific Products Co., Cat. No. P1126-8, and other suppliers.)

6.6.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup 20 mL ethyl alcohol preservative must be added to each liter of ether.

6.7 Stock standard solutions (1.00 µg/µL) - Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.7.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.7.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Quality control check standards that can be used to determine the accuracy of calibration standards will be available for the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

6.7.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicate a problem.

7. Calibration

7.1 Establish gas chromatographic operating parameters to produce retention times equivalent to those listed in Table 1. The GC chromatographic system may be calibrated using the external standard technique (Section 7.2) or the internal standard technique (Section 7.3).

7.2 External standard calibration procedure.

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with hexane. One of the external standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.2.2 Using injections of 2 to 5 µL of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to amount injected (calibration factor) is a constant over the working range (< 10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that compound.

7.3 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with hexane. One of the standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2 Using injections of 2 to 5 µL of each calibration standard, tabulate peak height or area responses against concentration for each compound and internal standard, and calculate response factors (RF) for each compound using equation 1.

$$\text{Eq. 1} \quad RF = (A_s C_{is})/(A_{is} C_s)$$

where:

A_s = Response for the parameter to be measured.
A_{is} = Response for the internal standard.
C_{is} = Concentration of the internal standard, (µg/L).
C_s = Concentration of the parameter to be measured, (µg/L).

If the RF value over the working range is a constant (< 10% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, vs. RF.

7.3.3 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

7.4 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

7.5 The cleanup procedure in Section 11 utilizes Florisil column chromatography. Florisil from different batches or sources may vary in adsorption capacity. To standardize the amount of Florisil which is used, the use of lauric acid value[7] is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per gram Florisil. The amount of Florisil to be used for each column is calculated by dividing 110 by this ratio and multiplying by 20 g.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within accuracy and precision limits expected of the method.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of the rapid advances that are occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such modifications are made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 The laboratory must spike and analyze a minimum of 10% of all samples to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 Select a representative spike concentration for each compound to be measured. Using stock standards, prepare a quality control check sample concentrate in acetone 1000 times more concentrated than the selected concentrations. Quality control check sample concentrates, appropriate for use with this method, will be available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

8.2.2 Using a pipet, add 1.00 mL of the check sample concentrate to each of a minimum of four 1000-mL aliquots of reagent water. A representative wastewater may be used in place of the reagent water, but one or more additional aliquots must be analyzed to determine background levels, and the spike level must exceed twice the background level for the test to be valid. Analyze the aliquots according to the method beginning in Section 10.

8.2.3 Calculate the average percent recovery, (R), and the standard deviation of the percent recovery (s), for the results. Wastewater background corrections must be made before R and s calculations are performed.

8.2.4 Using Table 2, note the average recovery (X) and standard deviation (p) expected for each method parameter. Compare these to the calculated values for R and s. If $s > 2p$ or $|X-R| > 2p$, review potential problem areas and repeat the test.

8.2.5 The U.S. Environmental Protection Agency plans to establish performance criteria for R and s based upon the results of interlaboratory testing. When they become available, these criteria must be met before any samples may be analyzed.

8.3 The analyst must calculate method performance criteria and define the performance of the laboratory for each spike concentration and parameter being measured.

8.3.1 Calculate upper and lower control limits for method performance.

$$\text{Upper Control Limit (UCL)} = R + 3s$$
$$\text{Lower Control Limit (LCL)} = R - 3s$$

where R and s are calculated as in Section 8.2.3. The UCL and LCL can be used to construct control charts[8] that are useful in observing trends in performance. The control limits above must be replaced by method performance criteria as they become available from the U.S. Environmental Protection Agency.

8.3.2 The laboratory must develop and maintain separate accuracy statements of laboratory performance for wastewater samples. An accuracy statement for the method is defined as $R \pm s$. The accuracy statement should be developed by the analysis of four aliquots of wastewater as described in Section 8.2.2, followed by the calculation of R and s. Alternately, the analyst may use four wastewater data points gathered through the requirement for continuing quality control in Section 8.4. The accuracy statements should be updated regularly[8].

8.4 The laboratory is required to collect a portion of their samples in duplicate to monitor spike recoveries. The frequency of spiked sample analysis must be at least 10% of all samples or one sample per month, whichever is greater. One aliquot of the sample must be spiked and analyzed as described in Section 8.2. If the recovery for a particular parameter does not fall within the control limits for method performance, the results reported for that parameter in all samples processed as part of the same set must be qualified as described in Section 13.3. The laboratory should monitor the frequency of data so qualified to ensure that it remains at or below 5%.

8.5 Before processing any samples, the analyst should demonstrate through the analysis of a one-liter aliquot of reagent water, that all glassware and reagent interferences are under control. Each time a set of samples is extracted or there is a change in reagents, a laboratory reagent blank should be processed as a safeguard against laboratory contamination.

8.6 It is recommended that the laboratory adopt additional quality

assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as GC with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices[9] should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be a free as possible of Tygon and other potential sources of contamination.

9.2 The samples must be iced or refrigerated at 4°C from the time of collection until extraction. Fill the sample bottles and, if residual chlorine is present, add 80 mg of sodium thiosulfate per each liter of water. U.S. Environmental Protection Agency methods 330.4 and 330.5 may be used to measure the residual chlorine[10]. Field test kits are available for this purpose.

9.3 All samples must be extracted within 7 days and completely analyzed within 40 days of extraction[2].

10. Sample Extraction

10.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel.

10.2 Add 60 mL methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask.

10.3 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

10.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D if the requirements of Section 8.2 are met.

10.5 Pour the combined extract through a drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.6 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (60° to 65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

NOTE: Some of the haloethers are very volatile and significant losses will occur in concentration steps if care is not exercised. It is important to maintain a constant gentle evaporation rate and not to allow the liquid volume to fall below 1 to 2 mL before removing the K-D from the hot water bath.

10.7 Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip and replace the column. Raise the temperature of the water bath to 85 to 90°C. Concentrate the extract as in Section 10.6 except use hexane to prewet the column. When the apparent volume of liquid reaches 1 to 2 mL, remove the K-D and allow it to drain and cool at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane. A 5-mL syringe is recommended for this operation. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extracts will be stored longer than two days, they should be transferred to Teflon-sealed screw-cap bottles.

10.8 Determine the original sample volume by refilling the sample bottle to the mark and transferring the water to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Cleanup and Separation

11.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. The cleanup procedure recommended in this method has been used for the analysis of various clean waters and industrial effluents. If particular circumstances demand the use of an alternative cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of each compound of interest is no less than 85%.

11.2 Florisil column cleanup for haloethers:

11.2.1 Adjust the sample extract volume to 10 mL.

11.2.2 Place a charge (nominally 20 g, actual amount determined as in Section 7.5) of activated Florisil in a 19-mm ID chromatographic column. After settling the Florisil by tapping the column, add about one-half inch layer of anhydrous granular sodium sulfate to the top. Allow the Florisil to cool.

11.2.3 Pre-elute the column with 50 to 60 mL of petroleum ether. Discard the eluate and just prior to exposure of the sulfate layer to air, quantitatively transfer the sample extract into the column by decantation and subsequent petroleum ether washings. Discard the eluate. Just prior to exposure of the sodium sulfate layer to the air, begin eluting the column with 300 mL of ethyl ether/petroleum ether (6 + 94) (V/V). Adjust the elution rate to approx-

imately 5 mL/min and collect the eluate in a 500-mL K-D flask equipped with a 10-mL concentrator tube. This fraction should contain all of the haloethers.

11.2.4 Concentrate the fraction by K-D as in Section 10.6 except prewet the Snyder column with hexane. When the apparatus is cool, remove the column and rinse the flask and its lower joint into the concentrator tube with hexane. Adjust the volume to 10 mL. Analyze by GC (Section 12.)

12. Gas Chromatography

12.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. This table includes retention times and MDL that were obtained under these conditions. Examples of the parameter separations achieved by these columns are shown in Figures 1 and 2. Other packed columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met. Capillary (open-tubular) columns may also be used if the relative standard deviations of responses for replicate injections are demonstrated to be less than 6% and the requirements of Section 8.2 are met.

12.2 Calibrate the system daily as described in Section 7.

12.3 If the internal standard approach is being used, the analyst must not add the internal standard to sample extracts until immediately before injection into the instrument. Mix thoroughly.

12.4 Inject 2 to 5 μL of the sample extract using the solvent-flush technique[11]. Smaller (1.0 μL) volumes can be injected if automatic devices are employed. Record the extract volume to the nearest 0.1 mL and the volume injected to the nearest 0.05 μL, and the resulting peak size in area or peak height units.

12.5 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

12.6 If the response for the peak exceeds the working range of the system, dilute the extract and reanalyze.

12.7 If the measurement of the peak response is prevented by the presence of interferences, further cleanup is required.

13. Calculations

13.1 Determine the concentration of individual compounds in the sample.

13.1.1 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor in Section 7.2.2. The concentration in the sample can be calculated from equation 2.

Eq. 2 Concentration, $\mu g/L = \frac{(A)(V_t)}{(V_i)(V_s)}$

where:

A = Amount of material injected, in nanograms.
V_i = Volume of extract injected (μL).
V_t = Volume of total extract (μL).
V_s = Volume of water extracted (mL).

13.1.2 If the internal standard calibration procedure was used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.3.2 and equation 3.

Eq. 3 Concentration, $\mu g/L = \frac{(A_s)(I_s)}{(A_{is})(RF)(V_o)}$

where:

A_s = Response for the parameter to be measured.
A_{is} = Response for the internal standard.
I_s = Amount of internal standard added to each extract (μg).
V_o = Volume of water extracted, in liters.

13.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

13.3 For samples processed as part of a set where the laboratory spiked sample recovery falls outside of the control limits in Section 8.4, data for the affected parameters must be labeled as suspect.

14. Method Performance

14.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero[11]. The MDL concentrations listed in Table 1 were obtained using reagent water[12]. Similar results were achieved using representative wastewaters.

14.2 This method has been tested for linearity of recovery from spiked reagent water and has been demonstrated to be applicable for the concentration range from 4X MDL to 1000 x MDL[12].

14.3 In a single laboratory (Monsanto Research Center), using spiked wastewater samples, the average recoveries presented in Table 2 were obtained[12]. Each spiked sample was analyzed in triplicate on three separate occasions. The standard deviation of the percent recovery is also included in Table 2.

14.4 The U.S. Environmental Protection Agency is in the process of conducting an interlaboratory method study to fully define the performance of this method.

References

1. See Appendix A.
2. "Determination of Haloethers in Industrial and Municipal Wastewaters." Report for EPA Contract 68-03-2633 (In preparation).
3. ASTM Annual Book of Standards, Part 31, D 3694. "Standard Practice for Preparation of Sample Containers and for Preservation," American Society for Testing and Materials, Philadelphia, PA, p. 679, 1980.
4. "Carcinogens - Working With Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, Aug. 1977.
5. "OSHA Safety and Health Standards, General Industry," (29CFR1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).
6. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

7. Mills, P.A., "Variation of Florisil Activity: Simple Method for Measuring Absorbent Capacity and Its Use in Standardizing Florisil Columns," *Journal of the Association of Official Analytical Chemists*, 51, 29 (1968).

8. "Handbook of Analytical Quality Control in Water and Wastewater Laboratories," EPA-600/4-79-019, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1979.

9. ASTM Annual Book of Standards, Part 31, D 3370, "Standard Practice for Sampling Water," American Society for Testing and Materials, Philadelphia, PA, p. 76, 1980.

10. "Methods 330.4 (Titrimetric, DPD-FAS) and 330.5 (Spectrophotometric, DPD) for Chlorine, Total Residual," Methods for Chemical Analysis of Water and Wastes, EPA 600-4/79-020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1979.

11. Burke, J. A., "Gas Chromatography for Pesticide Residue Analysis, Some Practical Aspects," *Journal of the Association of Official Analytical Chemists*, 48, 1037 (1965).

12. "EPA Method Validation Study 21 Method 611 (Haloethers)," Report for EPA Contract 68-03-2633 (In Preparation).

Table 1. Chromatographic Conditions and Method Detection Limits

Parameter	Retention Time (min.) Column 1	Retention Time (min.) Column 2	Method Detection Limit (µg/L)
Bis(2-chloroisopropyl) ether	8.4	9.7	0.8
Bis(2-chloroethyl) ether	9.3	9.1	0.3
Bis(2-chloroethoxy) methane	13.1	10.0	0.5
4-Chlorophenyl phenyl ether	19.4	15.0	3.9
4-Bromophenyl phenyl ether	21.2	16.2	2.3

Column 1 conditions: Supelcoport (100/120 mesh) coated with 3% SP-1000 packed in 1.8 m long x 2 mm ID glass column with helium carrier gas at a flow rate of 40 mL/min. Column temperature: 60°C for 2 min after injection then program at 8°C/min to 230°C and hold for 4 min. Under these conditions the retention time for Aldrin is 22.6 min.

Column 2 conditions: Tenax-GC (60/80 mesh) packed in a 1.8 m long x 2mm ID glass column with helium carrier gas at 40 mL/min flow rate. Column temperature: 150°C for 4 min after injection then program at 16°C/min to 310°C. Under these conditions the retention time for Aldrin is 18.4 min.

Table 2. Single Operator Accuracy and Precision

Parameter	Average Percent Recovery	Standard Deviation %	Spike Range (µg/L)	Number of Analyses	Matrix Types
Bis(2-chloroethyl)ether	59	4.5	97	27	3
Bis(2-chloroethoxy)methane	62	5.3	138	27	3
Bis(2-chloroisopropyl)ether	67	4.0	54	27	3
4-Bromophenyl phenyl ether	78	3.5	14	27	3
4-Chlorophenyl phenyl ether	73	4.5	30	27	3

Column: 3% SP-1000 on Supelcoport
Program: 60°C.-2 minutes 8°/minute to 230°C.
Detector: Hall electrolytic conductivity

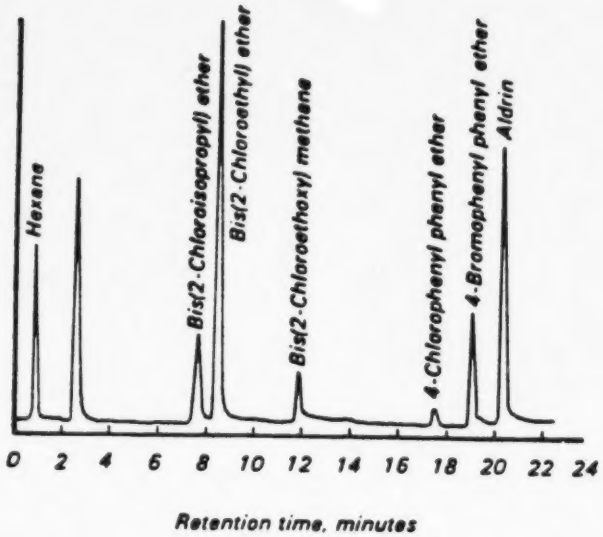

Figure 1. *Gas chromatogram of haloethers.*

Column: Tenax GC
Program: 150°C.-4 minutes 16°/minute to 310°C.
Detector: Hall electrolytic conductivity

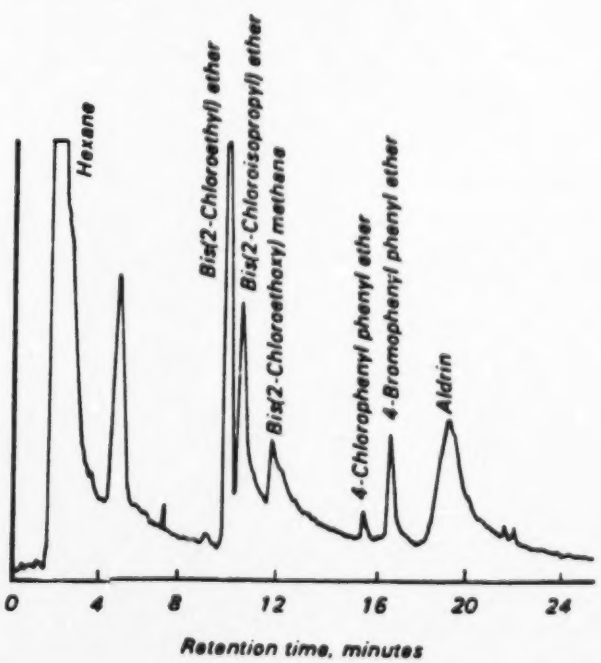

Figure 2. *Gas chromatogram of haloethers.*

APPENDIX B

RAW DATA

TABLE 18. RAW DATA FOR *BIS*(2-CHLOROISOPROPYL)ETHER BY WATER TYPE

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	1	5	1	5	1	5	1	5	1	5	1	5
TRUE CONC:	3.00	2.40	3.00	2.40	3.00	2.40	3.00	2.40	3.00	2.40	3.00	2.40
LAB NUMBER												
1	2.50	2.40	2.40	2.00	2.50	2.20	1.90	1.60	2.50	1.70	2.80	2.30
2	3.90	2.40	3.60	2.00	3.30	2.40	2.80	2.60	2.80	2.40	3.50	2.50
3	2.90	3.20	5.10	3.20	2.30	2.60	2.30	3.60	0.00*	0.00*	3.10	3.10
4	2.80	3.20	3.00	2.30	2.00	2.30	2.10	2.00	0.00*	0.00*	3.30	2.00
5	3.01	3.83	29.10*	21.60*	2.99	2.52	2.67	1.00	21.60*	25.20*	3.04	2.78
6	2.00	2.30	0.10	0.00*	0.70	0.50	1.00	0.00*	0.00*	0.00*	0.00*	0.00*
7	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.30
8	0.00*	0.00*	0.91	0.00*	0.00*	0.40	7.99	3.58	0.88	1.50	0.44	0.00*
9	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*
10	2.72	2.96	2.18	2.45	2.58	1.85	0.00*	0.00*	0.00*	0.00*	3.09	2.13
11	0.00*	8.20	3.00	0.00*	8.70	1.70	23.30*	51.00*	86.70*	37.50*	0.50	3.40
12	1.40*	0.48*	4.50	3.40	0.19	3.40	0.46	0.54	4.50	5.10	0.71	0.29
13	2.08	2.10	2.86	2.84	2.01	2.54	3.90	3.00	2.13	2.99	2.19	3.40
14	0.00*	3.71	3.59	3.30	3.55	3.02	2.82	2.69	0.00*	0.00*	3.89	3.14
15	8.00	6.20	7.00	5.60	7.00	8.10*	13.20	12.10	6.30	10.40	20.10*	5.80
16	5.20	4.80	7.80*	3.60*	3.20	3.20	10.30	10.10	0.00*	0.00*	4.20	2.50
17	13.63*	17.65*	12.18*	11.49*	13.70*	15.30*	0.00*	41.80*	0.00*	2.15	3.70	0.67
18	4.90	8.20	5.40	5.10	4.70	0.00*	4.70	4.60	0.00*	0.00*	4.60	4.20
19	9.10	1.00	0.00*	0.00*	2.50	1.50	3.20	5.80	46.10*	13.60	2.00	1.90
20	3.00	3.00	0.90	0.50	1.40	0.50	1.10	1.00	0.80	0.40	1.20	0.60

TABLE 18 (continued)

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	2	6	2	6	2	6	2	6	2	6	2	6
TRUE CONC:	132.00	92.00	132.00	92.00	132.00	92.00	132.00	92.00	132.00	92.00	132.00	92.00
LAB NUMBER												
1	120.00	73.00	120.00	81.00	100.00	79.00	88.00	52.00	130.00	88.00	110.00	75.00
2	146.00	93.00	146.00	89.00	150.00	92.00	159.00	91.00	167.00	81.00	149.00	91.00
3	60.00	78.00	117.00	84.00	107.00	74.00	95.00	54.00	136.00	100.00	116.00	58.00
4	132.00	94.00	120.00	89.00	120.00	94.00	109.00	94.00	125.00	82.00	125.00	84.00
5	136.00	80.00	103.00	94.60	108.00	76.70	124.00	82.40	135.00	98.70	96.60	67.70
6	143.00	112.00	280.00*	300.00*	109.00	160.00	158.00	97.00	211.00	190.00	210.00	164.00
7	197.30	111.20	157.30	91.10	72.00	167.50	299.00*	97.70	420.90*	339.20*	206.80	47.90
8	94.11	55.60	100.90	54.10	96.13	51.05	97.19	25.62	103.70	51.52	94.11	55.60
9	128.70	112.50	103.40	77.80	57.70	91.80	90.90	77.20	69.90	136.40	69.40	108.40
10	94.50	77.10	98.80	76.10	87.70	69.30	83.20	73.10	80.30	60.60	90.00	72.50
11	11.80	221.00*	128.00	161.00*	23.80	74.60	175.00	1670.00*	164.00	37.70	142.00	141.00
12	26.00*	36.00*	24.00	26.00	28.00	2.20	24.00	51.00	38.00	57.00	48.00	53.00
13	111.90	86.70	124.10	79.60	93.00	89.20	89.40	85.70	123.70	99.30	107.10	105.00
14	76.70	90.30	106.00	80.30	130.00	88.10	122.00	91.20	129.00	104.00	65.60	77.40
15	25.00	18.20	20.40	25.10	31.00	20.40	15.10	15.20	14.80	23.40	18.90	21.20
16	180.00	123.00	192.00*	129.00*	138.00	79.00	125.00	91.00	192.00	103.00	*	73.00
17	82.90	52.40	89.95	61.50	76.22	71.20	61.73	35.50	89.13	10.40	45.28	36.80
18	106.00	87.00	113.90	71.70	145.50	70.40	117.90	97.10	139.20	94.30	111.50	52.10
19	*	93.50	107.20	54.30	102.20	20.80	86.50	63.00	60.40	*	121.60	74.30
20	97.00	52.00	34.00	40.00	53.00	51.00	50.00	46.00	33.00	31.00	49.00	41.00

TABLE 18 (continued)

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	3	4	3	4	3	4	3	4	3	4	3	4
TRUE CONC:	486.00	624.00	486.00	624.00	486.00	624.00	486.00	624.00	486.00	624.00	486.00	624.00
LAB NUMBER												
1	470.00	610.00	430.00	540.00	250.00	540.00	380.00	470.00	430.00	560.00	430.00	590.00
2	575.00	671.00	653.00	714.00	651.00	757.00	642.00	610.00	670.00	711.00	661.00	757.00
3	464.00	446.00	371.00	390.00	348.00	530.00	335.00	306.00	394.00	512.00	420.00	652.00
4	520.00	570.00	500.00	610.00	450.00	700.00	485.00	640.00	470.00	600.00	490.00	700.00
5	517.00	513.00	402.00	558.00	438.00	589.00	432.00	477.00	506.00	673.00	421.00	533.00
6	340.00	510.00	420.00	650.00	610.00	540.00	380.00	540.00	550.00	770.00	545.00	640.00
7	775.70	832.00	652.40	791.20	674.20	1307.00*	743.30	858.10	1133.00	1232.00*	1019.00*	1448.00*
8	349.50	507.40	378.60	457.60	361.20	448.20	313.50	462.20	391.10	462.30	419.20	481.70
9	275.50	328.30	307.10	506.90	307.00	430.70	280.50	364.40	374.30	303.20	352.00	421.20
10	392.00	469.00	462.00	464.00	371.00	491.00	310.00	466.00	398.00	474.00	366.00	485.00
11	680.00	244.00	588.00	616.00	206.00	594.00	194.00	446.00	1120.00	515.00	571.00	614.00
12	106.00*	46.00*	284.00	393.00	197.00	379.00	213.00	129.00	207.00	243.00	218.00	395.00
13	393.80	572.00	452.70	628.00	425.30	643.00	407.10	596.10	520.40	549.20	521.10	605.80
14	479.00	565.00	385.00	592.00	422.00	560.00	410.00	478.00	361.00	395.00	319.00	415.00
15	75.00	81.00	63.90	95.00	89.00	48.80	110.00	100.80	93.00	62.90	105.00	65.00
16	400.00	589.00	856.00*	916.00*	452.00	582.00	329.00	605.00	425.00	593.00	431.00	571.00
17	519.60	515.70	440.40	547.00	555.60	389.00	487.60	552.80	302.50	436.10	247.10	651.30
18	392.90	596.00	414.80	650.20	581.30	584.60	376.80	504.80	510.20	456.50	258.30	340.00
19	667.60	*	110.80	*	30.20	41.80	86.50	741.00	283.00	381.60	292.40	923.20
20	230.00	400.00	180.00	160.00	210.00	220.00	160.00	190.00	140.00	120.00	170.00	180.00

TABLE 19. RAW DATA FOR *BIS*(2-CHLOROETHYL)ETHER BY WATER TYPE

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	1	5	1	5	1	5	1	5	1	5	1	5
TRUE CONC:	1.40	1.60	1.40	1.60	1.40	1.60	1.40	1.60	1.40	1.60	1.40	1.60
LAB NUMBER												
1	1.30	1.50	1.40	1.40	1.30	1.50	1.20	1.20	13.00	14.00	1.50	1.60
2	1.10	1.20	1.10	1.10	1.30	1.50	1.00	1.40	1.10	0.00*	1.30	1.60
3	1.10	1.30	2.00	1.60	0.80	1.20	1.10	1.10	0.00*	0.00*	1.20	0.80
4	0.60	0.70	1.10	0.70	10.00*	0.50	1.10	1.30	0.00*	0.00*	1.00	1.00
5	1.83	1.89	1.13	2.68	1.48	1.61	2.63	1.13	22.60	24.30	1.01	1.29
6	0.30	0.00*	0.00*	0.40	0.10	0.40	0.40	0.10	6.00	9.00	0.40	0.30
7	0.00*	0.00*	0.00*	0.00*	3.10	0.00*	0.00*	0.00*	0.00*	0.80	0.00*	1.20
8	0.00*	0.86	0.00*	0.00*	0.00*	0.00*	1.17	0.00*	2.40	1.38	0.17	0.00*
9	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*
10	0.90	1.56	0.90	1.47	0.69	0.88	0.61	1.37	0.00*	0.00*	1.03	0.90
11	0.00*	0.70*	3.20	2.10	0.70	2.20	3.40*	20.40*	8.40	13.20	0.10	0.80
12	0.40*	0.13*	1.90	0.58	0.09	1.00	0.55	0.40	1.90	4.30	0.27*	0.13*
13	1.10	1.73	1.17	1.40	1.09	1.32	1.49	2.20	1.10	1.90	1.25	1.18
14	0.00*	2.21	1.54	1.54	1.62	1.75	1.30	1.63	13.90	10.40	1.92	1.79
15	7.90*	6.90	8.80*	6.00*	9.00*	6.50*	9.10*	8.90*	6.10	6.30	6.00*	8.60*
16	2.40	2.60	3.20*	1.70*	1.10	1.50	1.70	2.10	22.00	9.30	2.50	1.20
17	3.70*	7.72	4.50*	9.23*	4.23	8.10*	5.63*	66.30*	0.00*	0.00*	2.85	4.38*
18	1.40	4.20	2.90	3.30	3.60	3.40*	1.80	1.90	1.80	0.00*	1.30	1.60
19	1.40	0.70	0.00*	0.00*	1.60	1.20	1.30	1.30	16.40	9.20	1.40	1.40
20	1.40	1.00	1.00	0.80	0.90	1.30	1.00*	0.90*	0.80*	0.60*	0.90	1.20

TABLE 19 (continued)

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	2	6	2	6	2	6	2	6	2	6	2	6
TRUE CONC:	108.00	87.00	108.00	87.00	108.00	87.00	108.00	87.00	108.00	87.00	108.00	87.00
LAB NUMBER												
1	72.00	65.00	97.00	74.00	79.00	69.00	69.00	43.00	110.00	77.00	81.00	63.00
2	116.00	72.00	114.00	66.00	129.00	66.00	126.00	73.00	126.00	78.00	126.00	78.00
3	57.00	75.00	113.00	84.00	89.00	67.00	87.00	57.00	110.00	91.00	93.00	54.00
4	115.00	82.00	98.00	77.00	110.00	86.00	90.00	72.00	120.00	84.00	105.00	88.00
5	99.20	66.30	72.50	74.60	82.20	67.10	94.80	69.30	94.00	79.30	76.70	59.90
6	85.00	70.00	93.00	100.00	53.00	84.00	73.00	51.00	76.00	70.00	79.00	57.00
7	133.40	91.50	121.50	85.00	65.60	153.00*	241.10*	155.40*	167.30	121.50	137.50	72.10
8	76.24	52.73	82.39	62.84	78.78	66.91	7.62	24.64	82.35	51.44	76.24	52.73
9	61.80	73.20	56.30	58.30	44.70	25.70	40.80*	22.90*	17.70*	20.40*	40.70	59.00
10	60.80	69.60	58.60	62.90	63.20	64.20	58.70	65.80	60.80	55.90	64.60	61.60
11	25.70*	26.00*	34.20	59.40	15.50	45.90	57.20	298.00*	55.40	47.40	38.70	51.20
12	20.00*	34.00*	18.00	18.00	19.00	1.50	22.00	40.00	38.00	38.00	34.00*	36.00*
13	93.70	89.50	100.30	83.50	94.70	81.30	90.20	97.40	110.80	84.90	108.00	100.00
14	56.00	74.90	81.50	68.60	97.90	75.10	91.40	75.40	111.00	93.30	56.60	64.20
15	40.10	25.40*	45.20	22.20	35.40	28.90	20.80	18.40	30.60	25.40	61.20	16.90
16	133.00	94.00	136.00*	93.00*	109.00	72.00	89.00	72.00	125.00	70.00	*	60.00
17	64.11	63.00	77.05	84.70	71.88	67.80	60.48	41.90	78.77	46.90	42.19	36.80
18	80.40	68.20	105.00	57.90	88.40	59.30	78.90	61.50	88.90	59.40	88.10	53.90
19	*	72.20	81.10*	34.70*	75.80	18.10	74.50	53.50	39.60	*	82.80	65.10
20	6.00	8.40*	12.00	10.00	16.00	9.00	16.00*	12.00*	11.00*	9.50*	19.00	11.00

TABLE 19 (continued)

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	3	4	3	4	3	4	3	4	3	4	3	4
TRUE CONC:	602.00	402.00	602.00	402.00	602.00	402.00	602.00	402.00	602.00	402.00	602.00	402.00
LAB NUMBER												
1	580.00	400.00	510.00	340.00	330.00	330.00	450.00	290.00	490.00	360.00	510.00	380.00
2	551.00	425.00	587.00	454.00	589.00	460.00	597.00	421.00	601.00	423.00	569.00	427.00
3	551.00	278.00	475.00	271.00	392.00	340.00	430.00	221.00	432.00	348.00	479.00	472.00
4	660.00	350.00	580.00	365.00	600.00	370.00	640.00	385.00	560.00	380.00	560.00	390.00
5	617.00	307.00	444.00	329.00	543.00	379.00	522.00	308.00	555.00	383.00	512.00	335.00
6	270.00	170.00	300.00	200.00	500.00	180.00	310.00	190.00	390.00	250.00	390.00	190.00
7	677.80	415.70	616.40	425.30	652.60	666.50	696.70	467.50	843.00	798.60*	823.00	581.00
8	456.00	332.10	486.90	294.20	453.00	288.50	392.10	323.30	444.40	304.50	508.20	331.70
9	237.90	146.10	255.30	246.60	310.80	151.90	264.80*	154.90*	382.20*	95.70*	328.70	144.80
10	574.00	290.00	541.00	323.00	403.00	303.00	358.00	285.00	476.00	323.00	441.00	303.00
11	150.00*	163.00*	137.00	168.00	72.00	182.00	4.40	200.00	127.00	226.00	101.00	268.00
12	123.00*	27.00*	315.00	228.00	208.00	285.00	218.00	106.00	181.00	132.00	238.00*	223.00*
13	480.70	379.70	603.40	423.10	495.00	435.40	509.30	399.40	599.30	351.60	609.00	418.90
14	520.00	367.00	473.00	417.00	568.00	391.00	467.00	322.00	466.00	290.00	452.00	284.00
15	76.00	89.50	70.10	68.90	38.00	72.30	82.00	92.00	110.00	43.10	92.00	61.00
16	454.00	358.00	876.00*	503.00*	569.00	359.00	440.00	355.00	501.00	346.00	519.00	326.00
17	695.00	400.90	539.40	413.20	769.90	314.30	704.20	367.90	391.40	451.00	367.60	409.60
18	472.30	352.00	478.50	385.30	540.80	350.70	438.60	363.10	466.10	229.60	438.70	280.40
19	581.50	*	68.90*	*	32.00	27.80	114.80	438.90	260.10	228.60	330.50	549.30
20	370.00	410.00	80.00	100.00	91.00	70.00	90.00*	71.00*	53.00*	51.00*	73.00	66.00

TABLE 20. RAW DATA FOR *BIS*(2-CHLOROETHOXY)METHANE BY WATER TYPE

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	1	5	1	5	1	5	1	5	1	5	1	5
TRUE CONC:	1.40	1.00	1.40	1.00	1.40	1.00	1.40	1.00	1.40	1.00	1.40	1.00
LAB NUMBER												
1	1.10	0.90	0.70	0.80	1.10	0.80	1.20	1.30	2.20	1.80	2.10	1.00
2	0.50	0.60	0.50	0.70	0.50	0.60	0.50	0.50	0.00*	0.70	0.40	0.70
3	0.50	0.60	1.50	0.80	0.70	0.50	1.10	0.40	0.00*	0.00*	2.00	1.00
4	1.00	1.50	0.70	0.50	1.40	0.30	1.50	0.90	1.40	1.40	1.10	1.10
5	1.96	0.99	1.42	1.06	1.88	1.66	1.46	1.78	1.34	8.50	0.88	1.20
6	0.40*	0.00*	0.00*	0.10*	0.30	0.30	0.40	0.00*	0.00*	0.00*	0.30	0.20
7	0.00*	0.00*	2.60	1.30	0.00*	0.00*	0.20	0.00*	0.00*	0.50	0.00*	0.00*
8	0.57	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.69	0.00*	0.00*	0.00*
9	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*
10	0.93	0.79	0.88	0.81	0.52	0.38	0.38	0.25	1.00	0.82	1.24	0.25
11	0.00*	0.00*	0.00*	0.00*	2.00	0.00*	17.20*	6.20*	8.00	4.00	2.60	0.00*
12	0.30*	0.14*	0.43	0.53	0.11	0.74	0.45	0.18	1.60	1.40	1.50	0.78
13	1.38	0.96	1.05	0.70	1.18	0.81	2.00	1.60	1.59	1.10	1.90	1.82
14	0.00*	1.18	1.53	0.89	1.42	0.89	1.08	0.70	0.00*	0.00*	1.33	0.62
15	11.00*	8.30*	9.20*	6.00	8.30*	7.10	11.00	12.00*	8.30	5.40	4.20	4.30
16	1.90	0.90	2.60	0.40	1.10	0.70	1.30	0.60	0.00*	0.00*	2.80	12.10*
17	3.38*	3.65*	5.10*	5.53	3.83*	6.43	6.95	2.78	0.95	2.00	2.63	4.98
18	8.50*	5.10*	12.70*	12.70*	5.30*	12.60*	8.50	8.40*	8.70	9.20	14.90*	4.50
19	0.70	0.30	0.00*	0.00*	1.90	1.10	1.00	0.90	56.40*	0.00*	1.50	1.50
20	37.00*	39.00*	4.30*	6.00*	5.60*	3.20*	4.20*	4.20*	2.90*	5.20*	5.10*	5.90*

TABLE 20 (continued)

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	2	6	2	6	2	6	2	6	2	6	2	6
TRUE CONC:	106.00	126.00	106.00	126.00	106.00	126.00	106.00	126.00	106.00	126.00	106.00	126.00
LAB NUMBER												
1	76.00	68.00	83.00	110.00	59.00	93.00	72.00	76.00	79.00	85.00	63.00	62.00
2	92.00	102.00	102.00	92.00	96.00	108.00	94.00	108.00	95.00	115.00	101.00	118.00
3	44.00	90.00	54.00	78.00	72.00	80.00	70.00	68.00	85.00	105.00	82.00	68.00
4	97.00	114.00	90.00	114.00	102.00	125.00	85.00	105.00	100.00	116.00	98.00	120.00
5	81.50	94.60	62.80	104.00	69.20	92.60	83.20	95.50	88.90	112.00	61.50	90.70
6	40.00*	60.00*	31.00*	64.00*	37.00	70.00	66.00	81.00	74.00	97.00	61.00	80.00
7	118.70	113.40	103.50	109.20	48.60	191.70	225.00*	195.90*	167.20*	135.90	91.10	37.30
8	64.22	80.52	68.22	80.03	69.23	67.62	71.55	31.58	75.63	89.98	64.22	80.52
9	72.50	66.70	64.20	60.40	41.70	52.90	38.70*	40.10*	42.70	117.00	116.30	114.90
10	52.40	87.20	48.60	84.50	51.50	81.70	50.30	83.80	46.90	67.90	56.30	81.50
11	0.00*	70.00	18.40	135.00	3.30	11.40	83.10	453.00*	64.80	112.00	48.30	110.00
12	21.00*	52.00*	19.00	60.00	21.00	3.10	27.00	65.00	30.00	76.00	41.00	82.00
13	95.70	121.90	112.60	121.10	93.40	110.60	93.40	143.60	112.90	132.30	114.30	144.10
14	47.20	98.10	63.10	85.90	76.00	99.60	68.70	91.40	93.80	109.00	47.30	95.30
15	80.50	32.60	63.80	21.10	43.60	41.00	49.90	21.30	66.70	38.80	75.80	45.10
16	102.00	130.00	94.00	131.00	71.00	88.00	69.00	85.00	105.00	86.00	*	80.00
17	54.03	68.40	63.30	89.40	46.09	88.70	44.25	55.30	60.97	237.50*	33.17	51.50
18	68.30	105.80	77.90	87.60	93.70	85.70	74.00	80.10	94.40	63.70	67.10	88.30
19	*	69.10	75.70	56.70	71.90	25.60	75.90	57.00	33.90	*	70.10	77.70
20	460.00*	310.00*	180.00*	160.00*	280.00*	180.00*	290.00*	190.00*	180.00*	130.00*	240.00*	210.00*

TABLE 20 (continued)

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	3	4	3	4	3	4	3	4	3	4	3	4
TRUE CONC:	398.00	528.00	398.00	528.00	398.00	528.00	398.00	528.00	398.00	528.00	398.00	528.00
LAB NUMBER												
1	300.00	340.00	310.00	340.00	170.00	290.00	270.00	350.00	290.00	410.00	310.00	430.00
2	302.00	470.00	340.00	378.00	254.00	446.00	363.00	531.00	342.00	599.00	328.00	460.00
3	305.00	253.00	143.00	233.00	270.00	435.00	238.00	259.00	315.00	402.00	240.00	396.00
4	410.00	470.00	360.00	480.00	400.00	500.00	380.00	550.00	400.00	580.00	390.00	520.00
5	438.00	410.00	279.00	409.00	364.00	502.00	334.00	381.00	349.00	474.00	312.00	408.00
6	10.00*	120.00*	80.00*	150.00*	160.00	130.00	70.00	130.00	130.00	220.00	140.00	160.00
7	436.80	483.50	388.60	459.90	402.30	727.60	502.90	610.10	435.30	838.40	472.70	755.70
8	289.90	443.70	308.60	393.80	294.20	399.00	260.80	402.10	321.60	411.10	336.20	426.80
9	148.10	228.10	170.60	263.50	193.50	279.70	184.30*	205.80*	288.20	179.80	247.20	333.50
10	256.00	342.00	269.00	323.00	233.00	338.00	219.00	315.00	262.00	332.00	255.00	327.00
11	152.00	69.00	162.00	172.00	8.30	180.00	97.10	297.00	151.00	336.00	131.00	440.00
12	98.00*	39.00*	224.00	336.00	168.00	350.00	207.00	135.00	149.00	217.00	224.00	65.00
13	313.90	541.60	399.40	572.20	353.10	581.40	369.60	580.20	385.20	515.00	372.30	499.30
14	339.00	425.00	296.00	467.00	393.00	446.00	307.00	402.00	270.00	303.00	205.00	322.00
15	98.00	53.50	83.10	65.10	95.00	63.10	63.00	68.40	83.00	120.10	38.00	110.50
16	245.00	346.00	521.00	559.00	282.00	352.00	213.00	370.00	271.00	434.00	219.00	347.00
17	311.60	428.10	242.60	471.00	333.40	329.60	306.10	425.20	162.20	484.10	144.10	513.80
18	293.30	468.10	292.50	444.40	436.50	459.30	288.00	474.50	314.90	338.60	249.70	370.50
19	362.50	*	79.00	*	21.20	30.30	75.00	533.90	178.60	243.60	170.40	562.30
20	380.00*	520.00*	500.00*	600.00*	610.00*	1000.00*	450.00*	910.00*	460.00*	580.00*	470.00*	950.00*

TABLE 21. RAW DATA FOR 4-CHLOROPHENYL PHENYL ETHER BY WATER TYPE

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	1	5	1	5	1	5	1	5	1	5	1	5
TRUE CONC:	14.50	6.60	14.50	6.60	14.50	6.60	14.50	6.60	14.50	6.60	14.50	6.60
LAB NUMBER												
1	9.80	6.40	12.00	6.30	12.00	5.80	12.00	5.10	19.00	14.00	13.00	6.50
2	14.00	6.90	15.00	5.20	15.00*	8.30*	15.00*	8.30*	16.00	7.50	14.00*	9.50*
3	6.70	4.30	11.10	5.90	7.00	5.00	6.50	2.50	0.00*	0.00*	11.80	7.40
4	15.20	8.70	11.50	6.00	16.50	5.80	17.00	9.20	28.00	23.00	15.00	8.40
5	20.30	7.99	11.50	7.86	11.90	5.74	14.20	4.80	16.40	12.00	12.80	8.61
6	1.30*	0.00*	1.70	2.10	4.40	2.10	6.30	15.00*	70.00	107.00	8.10	9.00
7	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.80	0.00*	0.30	0.00*	0.60	0.00*
8	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	6.07	9.11	1.97	0.00*
9	15.20	6.90	15.60	7.00	11.00	6.90	12.10	7.60	0.00*	0.00*	0.00*	0.00*
10	5.04	3.95	5.02	2.47	5.22	2.51	1.67	2.75	3.37	0.00*	2.00	2.53
11	0.00*	0.00*	1.50	0.60	3.50*	1.70*	5.50	6.70	53.00	42.40	1.90	0.00*
12	2.80*	1.20*	18.00	5.20	1.10	5.10	7.20	3.00	18.00	4.80	11.00	6.60
13	20.80*	13.50*	19.90*	14.80*	18.00*	13.90*	19.40*	13.30*	19.30*	14.20*	23.00*	13.40*
14	0.00*	12.30	15.20	7.40	13.80	6.99	7.57	3.64	17.10	12.80	14.80	6.44
15	13.00	10.00	10.50	8.90	12.20	8.60	15.00	6.60	4.90	7.10	8.00	12.00
16	23.50	11.50	28.10*	7.30*	12.50	7.10	16.30	7.20	24.50	7.40	18.40	6.40
17	45.03*	39.23*	44.35*	42.33*	40.05*	34.05*	36.08*	23.93*	7.46	96.32	21.00	30.75*
18	10.00	11.80	16.70	12.10	13.10	11.90	13.30	10.10	14.80	9.80	9.10	1.30
19	21.80	5.90	0.00*	0.00*	9.90	4.20	3.50	3.30	56.40	27.50	8.70	5.00
20	0.40	1.30	6.00	3.30	3.90	4.10	5.20	4.10	4.00	2.60	4.90	3.80

TABLE 21 (continued)

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	2	6	2	6	2	6	2	6	2	6	2	6
TRUE CONC:	94.00	120.00	94.00	120.00	94.00	120.00	94.00	120.00	94.00	120.00	94.00	120.00
LAB NUMBER												
1	74.00	93.00	83.00	100.00	74.00	96.00	71.00	91.00	88.00	100.00	74.00	92.00
2	143.00	158.00	141.00*	154.00	138.00*	158.00*	140.00*	158.00*	141.00	165.00	145.00*	159.00*
3	40.00	95.00	63.00	88.00	67.00	87.00	59.00	59.00	81.00	93.00	76.00	68.00
4	97.00	118.00	88.00	115.00	104.00	125.00	81.00	109.00	100.00	112.00	100.00	120.00
5	90.30	103.00	65.50	112.00	57.00	78.30	86.00	101.00	69.80	92.20	67.40	83.70
6	33.00*	66.00*	49.00	132.00	32.00	103.00	45.00	49.00	74.00	113.00	76.00	100.00
7	114.00	123.40	82.70	105.10	44.10	213.40*	141.10	126.20	58.30	69.00	115.40	22.50
8	59.60	89.21	65.43	84.23	75.56	79.73	54.36	30.79	78.99	68.19	59.60	89.21
9	126.60	115.80	102.40	103.20	93.60	119.00	122.50	76.40	86.00	329.70*	214.40*	239.70*
10	68.80	115.00	73.20	118.00	64.50	111.00	64.50	115.00	67.20	86.10	70.20	108.00
11	18.50	91.10	46.70	38.40	11.80*	35.00*	68.10	515.00*	36.30	25.90	27.70	40.00
12	24.00*	42.00*	26.00	88.00	34.00	6.60	18.00	95.00	34.00	73.00	75.00	117.00
13	110.80*	169.70*	129.10*	164.20*	106.50*	161.30*	115.70*	186.10*	123.70*	174.00*	153.60*	163.30*
14	34.00	126.00	74.30	93.10	88.70	101.00	73.80	101.00	82.30	110.00	57.30	125.00
15	100.20	88.30	69.60	45.00	55.60	32.20	56.10	93.20	120.20	63.10	83.00	38.20
16	114.00	161.00	120.00*	183.00*	89.00	110.00	79.00	108.00	89.00	109.00	*	96.00
17	60.80	56.70	60.70	60.60	47.39	74.40	30.74	46.40	44.51	53.90	30.29	49.70
18	64.00	106.40	97.80	117.50	83.80	95.40	60.90	45.90	84.70	63.50	81.50	72.00
19	*	116.90	64.60*	72.10*	57.10	24.10	101.20	60.50	39.70	*	69.30	93.20
20	36.00	41.00	70.00	51.00	61.00	54.00	62.00	46.00	130.00	41.00	48.00	53.00

TABLE 21 (continued)

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	3	4	3	4	3	4	3	4	3	4	3	4
TRUE CONC:	489.00	424.00	489.00	424.00	489.00	424.00	489.00	424.00	489.00	424.00	489.00	424.00
LAB NUMBER												
1	440.00	330.00	460.00	390.00	260.00	340.00	390.00	340.00	390.00	390.00	380.00	390.00
2	703.00	712.00	750.00	670.00	768.00*	678.00*	712.00*	662.00*	683.00	621.00	740.00*	682.00*
3	441.00	294.00	418.00	280.00	411.00	389.00	317.00	252.00	345.00	363.00	388.00	540.00
4	550.00	480.00	530.00	500.00	398.00	490.00	395.00	560.00	450.00	530.00	428.00	510.00
5	484.00	309.00	407.00	379.00	380.00	346.00	424.00	335.00	654.00	356.00	435.00	388.00
6	120.00*	130.00*	170.00	70.00	250.00	130.00	130.00	190.00	230.00	130.00	230.00	160.00
7	645.70	480.00	561.90	403.00	594.30	813.40*	581.90	472.90	441.10	410.30	854.30*	880.90*
8	340.80	375.20	417.90	329.40	421.20	325.70	261.50	254.50	404.90	248.10	439.90	351.00
9	388.60	187.50	411.00	482.40	545.30	384.10	360.20	322.60	579.90	349.40	587.90	552.80
10	169.00	167.00	169.00	144.00	169.00	163.00	160.00	174.00	183.00	171.00	186.00	164.00
11	272.00	207.00	240.00	202.00	129.00*	195.00*	41.50	145.00	291.00	166.00	291.00	208.00
12	84.00*	55.00*	211.00	244.00	208.00	310.00	269.00	135.00	228.00	244.00	198.00	262.00
13	588.40*	600.00*	682.50*	647.00*	591.20*	606.00*	599.70*	600.90*	621.50*	599.00*	613.90*	508.70*
14	450.00	420.00	373.00	394.00	466.00	398.00	389.00	361.00	209.00	173.00	373.00	384.00
15	160.00	63.00	150.00	83.10	210.00	84.20	110.00	53.20	200.00	210.40	151.00	106.80
16	431.00	407.00	815.00*	575.00*	462.00	357.00	332.00	340.00	417.00	450.00	370.00	358.00
17	470.50	294.30	360.20	351.00	436.30	226.70	262.50	228.30	123.10	216.40	208.40	359.60
18	473.80	498.70	496.30	451.50	458.90	450.00	334.60	314.00	414.60	210.30	385.60	341.70
19	477.70	*	112.30*	*	33.90	36.40	211.20	143.80	355.60	419.00	239.20	552.30
20	120.00	180.00	150.00	150.00	210.00	180.00	230.00	400.00	130.00	120.00	220.00	160.00

TABLE 22. RAW DATA FOR 4-BROMOPHENYL PHENYL ETHER BY WATER TYPE

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	1	5	1	5	1	5	1	5	1	5	1	5
TRUE CONC:	2.80	3.80	2.80	3.80	2.80	3.80	2.80	3.80	2.80	3.80	2.80	3.80
LAB NUMBER												
1	1.90	3.60	2.50	3.70	1.70	4.00	2.90	3.30	3.10	4.00	3.10	4.30
2	2.40	4.30	1.80	2.30	1.80	4.70	2.00	2.70	2.00	3.70	0.00*	3.30
3	4.00	3.90	6.00	5.10	4.30	4.80	3.70	2.50	0.00*	0.00*	8.50	6.40
4	3.60	7.00	3.40	4.20	5.60	4.50	8.20	8.20	12.50*	12.50	4.50	4.80
5	6.66	7.25	3.60	6.82	5.43	6.19	4.41	5.77	13.50*	30.20*	4.58	6.86
6	0.00*	0.00*	0.00*	0.90	2.20	0.40	7.00	2.00	2.00	4.00	2.30	2.30
7	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	1.20	0.00*	1.87	0.00*	0.80	0.00*
8	0.00*	0.00*	0.00*	0.00*	0.00*	6.29	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*
9	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*
10	2.44	2.85	2.65	2.47	2.98	2.45	0.00*	2.56	2.17	2.57	2.17	1.98
11	0.00*	0.00*	0.00*	0.00*	11.60	7.00	8.60	57.10*	4.30	220.00*	4.30	5.50
12	0.15	0.42	1.40	4.20	0.96	2.70	1.30	2.00	1.10	0.75	1.60	0.48
13	3.43	10.20	2.81	8.40	3.06	8.34	3.86	9.10	3.94	8.39	3.94	8.65
14	0.00*	9.65	3.80	5.21	3.35	5.40	3.35	4.04	6.74	16.10	6.74	4.09
15	8.00	9.00	8.00	10.00	10.10	9.00	4.00	8.30	6.00	5.50	6.00	6.30
16	5.70	7.00	6.20*	9.60*	3.00	3.60	4.00	5.50	7.70	13.00	7.70	4.80
17	7.45	22.28*	6.23	21.13*	6.65	16.63*	6.13	10.00	3.70	14.38	3.70	17.98*
18	9.30	8.10	8.80	10.50	4.10	9.60	9.50	9.90	1.20	8.50	1.20	0.00*
19	5.00	9.50	0.00*	0.00*	3.40	4.50	1.10	2.00	4.30	0.00*	4.30	5.00
20	0.80*	1.30*	2.80	1.80	3.00	1.90	2.50	2.10	2.70	1.80	2.70	1.90

TABLE 22 (continued)

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	2	6	2	6	2	6	2	6	2	6	2	6
TRUE CONC:	145.00	116.00	145.00	116.00	145.00	116.00	145.00	116.00	145.00	116.00	145.00	116.00
LAB NUMBER												
1	120.00	85.00	130.00	110.00	120.00	100.00	120.00	96.00	120.00	89.00	130.00	94.00
2	192.00	113.00	184.00	113.00	203.00	117.00	197.00	117.00	213.00	128.00	216.00	129.00
3	65.00	98.00	93.00	89.00	103.00	89.00	89.00	61.00	120.00	89.00	110.00	67.00
4	135.00	104.00	145.00	128.00	155.00	148.00	134.00	118.00	145.00	118.00	148.00	125.00
5	139.00	113.00	112.00	125.00	97.30	100.00	151.00	103.00	159.00*	139.00*	91.80	83.70
6	71.00	70.00	85.00	96.00	46.00	80.00	118.00	66.00	100.00	108.00	120.00	81.00
7	245.80	166.40	185.90	161.40	103.80	197.60	286.60	271.80*	272.30	226.80*	235.10	20.20
8	95.93	57.90	100.80	47.66	102.50	60.43	77.47	153.40	118.80	46.14	95.93	57.90
9	266.40	64.30	257.90	48.60	246.50	82.30	226.20	44.60	262.80	366.70*	428.60*	195.60
10	198.00	200.00	215.00	210.00	189.00	188.00	189.00	205.00	191.00	86.50	181.00	194.00
11	69.00	116.00	74.00	49.00	68.00	50.00	99.10	436.00*	247.00	31.40	63.00	83.00
12	37.00	39.00	35.00	84.00	45.00	2.20	26.00	89.00	50.00	88.00	101.00	112.00
13	134.70	128.20	149.10	112.50	120.10	113.30	139.80	134.00	146.80	129.20	183.90	154.00
14	79.10	112.00	88.20	88.50	131.00	106.00	101.00	93.70	162.00	132.00	98.50	162.00
15	50.60	41.10	40.10	30.10	38.90	28.90	109.00	28.50	56.10	48.30	42.10	48.30
16	204.00	149.00	196.00*	166.00*	164.00	126.00	128.00	112.00	140.00	126.00	*	101.00
17	86.04	7.43	63.81	43.20	43.12	82.30	23.89	39.30	37.40	45.60	25.18	43.80
18	102.30	95.90	122.10	88.90	126.00	88.70	85.20	96.30	143.90	109.00	114.20	59.10
19	*	143.70	133.50	89.10	119.50	32.20	186.50	61.40	69.40	*	120.50	84.80
20	16.00*	23.00*	83.00	45.00	120.00	84.00	90.00	51.00	51.00	38.00	71.00	41.00

TABLE 22 (continued)

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	3	4	3	4	3	4	3	4	3	4	3	4
TRUE CONC:	552.00	626.00	552.00	626.00	552.00	626.00	552.00	626.00	552.00	626.00	552.00	626.00
LAB NUMBER												
1	550.00	550.00	500.00	560.00	330.00	470.00	490.00	550.00	420.00	510.00	480.00	600.00
2	526.00	694.00	554.00	747.00	534.00	673.00	547.00	691.00	561.00	621.00	519.00	773.00
3	487.00	397.00	475.00	380.00	483.00	562.00	333.00	176.00	361.00	450.00	431.00	558.00
4	510.00	540.00	690.00	760.00	640.00	670.00	575.00	610.00	500.00	610.00	690.00	770.00
5	528.00	415.00	447.00	530.00	405.00	466.00	472.00	470.00	586.00*	650.00*	413.00	463.00
6	130.00	180.00	160.00	200.00	320.00	170.00	160.00	240.00	200.00	230.00	200.00	240.00
7	927.50	874.30	835.10	820.70	875.50	1142.00	899.50	973.90	1101.00	1841.00*	1078.00*	1019.00
8	405.10	467.10	439.20	506.90	476.50	413.80	229.10	328.00	444.90	312.20	357.90	340.90
9	804.40	776.40	897.80	1089.00	1289.00*	692.40	460.90	471.70	1033.00	603.70	1340.00*	1133.00
10	410.00	465.00	388.00	448.00	411.00	451.00	487.00	475.00	448.00	470.00	439.00	464.00
11	338.00	338.00	282.00	320.00	113.00	310.00	606.00	237.00	296.00	302.00	99.00	343.00
12	138.00	63.00	519.00	536.00	394.00	626.00	405.00	258.00	315.00	182.00	328.00	556.00
13	499.30	679.30	572.80	651.00	526.00	706.00	575.30	637.10	539.80	627.30	509.30	541.90
14	572.00	609.00	505.00	613.00	583.00	584.00	455.00	532.00	396.00	405.00	429.00	520.00
15	150.00	39.00	121.00	63.00	160.00	39.10	95.00	66.10	100.00	73.80	160.00	65.00
16	538.00	733.00	1179.00*	995.00*	558.00	681.00	376.00	565.00	376.00	480.00	493.00	626.00
17	570.50	447.70	427.50	538.60	452.50	309.30	218.00	297.20	81.20	229.10	95.40	573.20
18	464.80	622.60	485.20	607.50	504.90	572.70	330.10	410.90	522.10	372.00	439.60	472.20
19	710.00	*	175.00	*	56.50	80.10	240.00	297.60	440.50	554.70	282.50	766.60
20	41.00*	91.00*	180.00	210.00	260.00	170.00	210.00	240.00	160.00	180.00	210.00	240.00

APPENDIX C

EFFECT OF WATER TYPE

TABLE 23. EFFECT OF WATER TYPE ON *BIS*(2-CHLOROISOPROPYL)ETHER ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = .89680

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	-.3272	.0554
3	-.5667	.0746
4	-.1527	.0082
5	-.0371	.0058
6	-.6058	.1057

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	2376.27654	2376.27654		
REG(WATER/DISTILLED)	10	8.72289	.87229	2.73	.0027
ERROR	586	187.24995	.31954		
TOTAL	597	2572.24938			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERCEPT(WATER-DISTILLED) INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	SLOPE(WATER-DISTILLED) INTERVAL
2	-.3272	(-.8410 , .1866)	.0554	(-.0512 , .1619)
3	-.5667	(-1.0530 , -.0805)	.0746	(-.0276 , .1768)
4	-.1527	(-.6469 , .3415)	.0082	(-.0950 , .1113)
5	-.0371	(-.6142 , .5400)	.0058	(-.1101 , .1216)
6	-.6058	(-1.0867 , -.1249)	.1057	(.0041 , .2073)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

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TABLE 24. EFFECT OF WATER TYPE ON *BIS*(2-CHLOROETHYL)ETHER ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = .95505

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	.0430	-.0148
3	-.2110	.0011
4	-.2705	.0133
5	1.5530	-.2841
6	-.3299	.0453

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	2677.86120	2677.86120		
REG(WATER/DISTILLED)	10	62.77067	6.27707	20.42	.0000
ERROR	567	174.27510	.30736		
TOTAL	578	2914.90698			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERCEPT(WATER-DISTILLED) INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	SLOPE(WATER-DISTILLED) INTERVAL
2	.0430	(-.4113 , .4972)	-.0148	(-.1116 , .0820)
3	-.2110	(-.6446 , .2225)	.0011	(-.0919 , .0942)
4	-.2705	(-.7154 , .1744)	.0133	(-.0823 , .1089)
5	1.5530	(1.0971 , 2.0088)	-.2841	(-.3814 , -.1868)
6	-.3299	(-.7598 , .1001)	.0453	(-.0477 , .1382)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

TABLE 25. EFFECT OF WATER TYPE ON *BIS*(2-CHLOROETHOXY)METHANE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = .97708

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	.1854	-.0324
3	.1120	-.0521
4	.1548	-.0307
5	.8987	-.1419
6	.4922	-.0820

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	2700.34836	2700.34836		
REG(WATER/DISTILLED)	10	15.96533	1.59653	4.71	.0000
ERROR	550	186.40293	.33891		
TOTAL	561	2902.71661			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERCEPT(WATER-DISTILLED) INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	SLOPE(WATER-DISTILLED) INTERVAL
2	.1854	(-.3145 , .6854)	-.0324	(-.1370 , .0722)
3	.1120	(-.3752 , .5993)	-.0521	(-.1540 , .0499)
4	.1548	(-.3303 , .6398)	-.0307	(-.1330 , .0716)
5	.8987	(.3902 , 1.4072)	-.1419	(-.2474 , -.0364)
6	.4922	(.0102 , .9742)	-.0820	(-.1832 , .0192)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

TABLE 26. EFFECT OF WATER TYPE ON 4-CHLOROPHENYL PHENYL ETHER ANALISIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = .98157

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	-.1713	.0254
3	-.0894	-.0189
4	-.1608	-.0071
5	.9987	-.1949
6	-.1895	.0227

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	1253.54913	1253.54913		
REG(WATER/DISTILLED)	10	15.57147	1.55715	4.87	.0000
ERROR	554	177.05007	.31958		
TOTAL	565	1446.17067			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERCEPT(WATER-DISTILLED) INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	SLOPE(WATER-DISTILLED) INTERVAL
2	-.1713	(-.8890 , .5464)	.0254	(-.1246 , .1754)
3	-.0894	(-.8067 , .6278)	-.0189	(-.1692 , .1315)
4	-.1608	(-.8691 , .5476)	-.0071	(-.1554 , .1412)
5	.9987	(.2979 , 1.6996)	-.1949	(-.3415 , -.0483)
6	-.1895	(-.9038 , .5248)	.0227	(-.1271 , .1724)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

TABLE 27. EFFECT OF WATER TYPE ON 4-BROMOPHENYL PHENYL ETHER ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = .87998

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	-.0451	.0171
3	.0025	-.0106
4	.0239	-.0114
5	.0935	-.0185
6	-.1010	.0205

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	2099.01021	2099.01021		
REG(WATER/DISTILLED)	10	.97749	.09775	.32	.9750
ERROR	602	182.02048	.30236		
TOTAL	613	2282.00818			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	INTERVAL
2	-.0451	(-.5696 , .4794)	.0171	(-.0894 , .1236)
3	.0025	(-.4921 , .4970)	-.0106	(-.1124 , .0912)
4	.0239	(-.4732 , .5211)	-.0114	(-.1134 , .0906)
5	.0935	(-.4234 , .6103)	-.0185	(-.1239 , .0869)
6	-.1010	(-.6019 , .3999)	.0205	(-.0824 , .1234)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

APPENDIX D

OTHER MC FINDINGS

Recovery and Reproducibility Studies (Worst Case Basis)

The industrial effluent selected (Wastewater D) contained several compounds (after extraction) which interfered with the haloether analysis. This effluent/wastewater was a "before treatment" sample which would be expected to have high levels of interferences present which would more typically be present in much lower concentrations in discharge waters. Ampul #5 of the method validation study was selected for spiking the wastewater. This solution contained the lowest haloether concentrations used in that study. This would therefore be a worse case study considering both concentration and interferences.

Eight 1-liter portions of the selected wastewater were used in this experiment. Seven of these portions were each spiked with 1 mL of Ampul #5 (see Table 28 for concentrations). The eighth portion was the blank. The samples were extracted and concentrated as described in the Federal Register method. They were analyzed using a Hall Model 310 detector (see Table 29 for conditions) with 5-μL manual injections. (The Model 310 detector is the least sensitive of the Hall detectors.) After they were analyzed, all samples were cleaned with Florisil, reconcentrated, and were again analyzed using the same conditions and injections as before. Figure 1 is the chromatogram of the Florisil cleaned blank, and Figure 2 is one of the spiked sample chromatograms.

The final relative standard deviations for the seven replicate samples in Table 28 are quite small, considering the severity of the experimental design. The wastewater had enough interfering compounds to truly test the Florisil cleanup. More importantly, the low haloether concentrations (ranging from 1 ppb to 6.6 ppb of wastewater) are near the present detection limits for this procedure. Small analyte losses during handling represent large relative losses, while at higher concentrations these same small losses would represent small relative losses. Table 28 also shows

TABLE 28. REPLICATION DATA

Compound	Spiking solution concentration, µg/L	7 Samples before cleanup[a] RSD[b], %	7 Samples before cleanup[a] Average recovery, %	7 Samples after cleanup[a] RSD[b], %	7 Samples after cleanup[a] Average recovery, %
BCIPE	2.4	-	ND[c]	-	ND[c]
BCEE	1.6	6.5	106[d]	9.3	91[d]
BCEXM	1.0	5.2	89	20.9	75
CPPE	6.6	6.4	88[d]	17.3	63
BPPE	3.8	19.3	93	20.6	78

[a]Cleanup with Florisil.

[b]RSD = relative standard deviation.

[c]None detected due to obscuring interference peak.

[d]Had some interference - values were determined by subtracting interference.

TABLE 29. CHROMATOGRAPHIC CONDITIONS FOR REPLICATION ANALYSES

Item	Description
Chromatograph	Hewlett-Parkard Model 5710A
Injection port temperature	250°C
Auxiliary transfer line	250°C
Column gas flow	30 mL/min UHP-grade helium
Column	1.8 m x 2.1 mm, glass, packed with 3% SP-1000 on Supelcoport (100/120 mesh)
Column program	100°C for 4 min, programmed at 16°C/min to 230°C
Hall 310 furnace	850°C
Hall electrolyte flow	0.5 mL/min, 50/50 ethyl alcohol/water
Hydrogen flow	70 mL/min
Conductivity range (µmho)	1
Attenuation	4

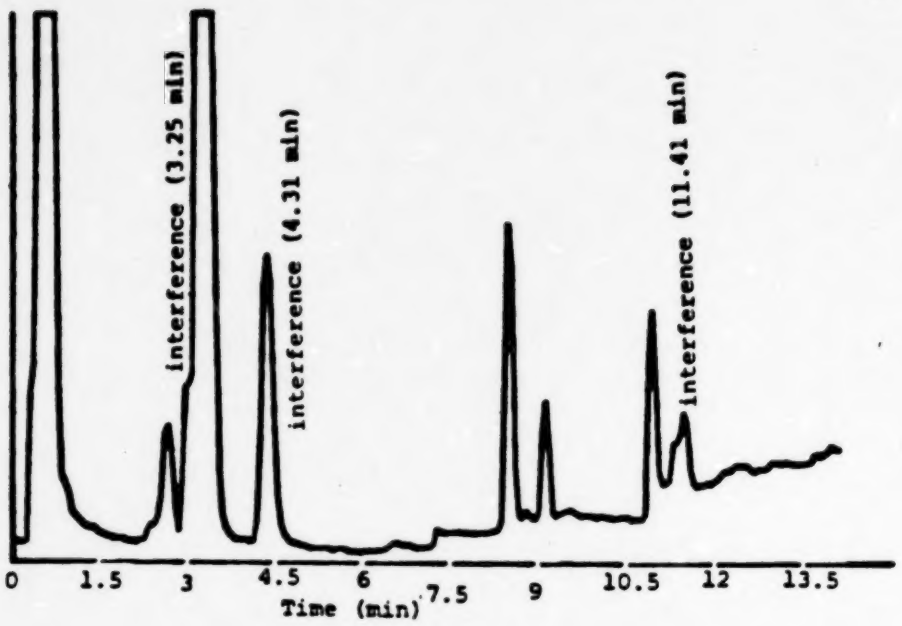

Figure 1. Chromatogram of wastewater blank extraction (after Florisil cleanup).

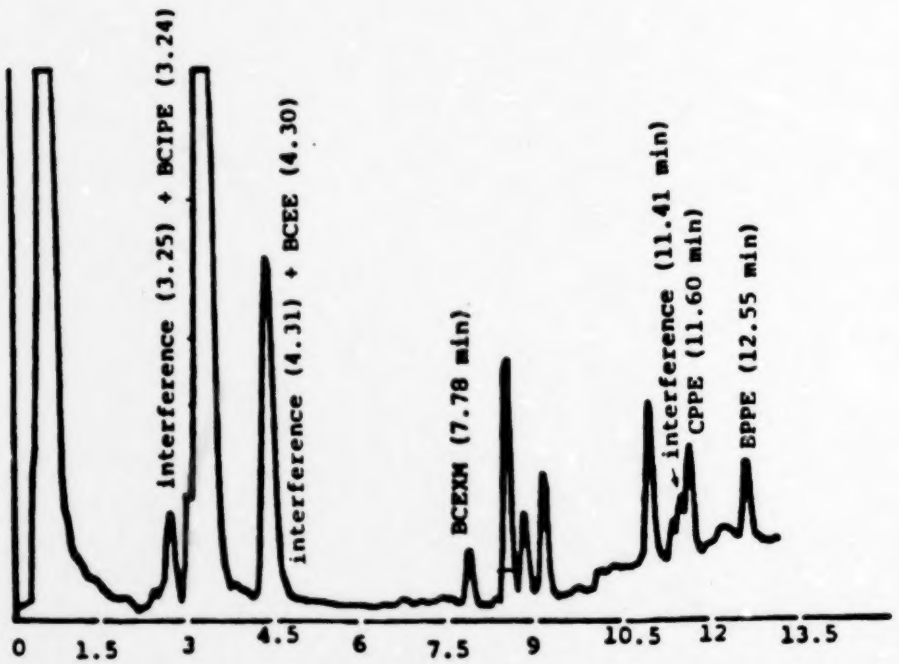

Figure 2. Chromatogram of spiked wastewater extraction.

that Florisil cleanup and the additional Kuderna-Danish concentration increase the analytical variation and decrease the percent recovery as would be expected from additional sampling handling.

The chromatograms in Figures 1 and 2 show the relationship of the haloether peaks to the interfering peaks which remained after Florisil cleanup. The BCIPE peak is completely obscured by the interfering compounds at 3.25 minutes. The additive effect of the BCEE spiking can be seen on the interference peak at 4.31 minutes. The rest of the haloethers are sufficiently separated from interferences to allow normal quantitation.

An average final recovery of 75-90% and a relative standard deviation of 10-20% for low ppb samples in a worse case wastewater or effluent demonstrates the high recovery and good reproducibility which could be expected in end-use applications of the method.

Clean-up Effectiveness and Interference Identification

Eight wastewaters including the three used for the method validation study (1, 2, and 3) were analyzed by Method 611 using both electrolytic conductivity and mass spectroscopic detection, before and after Florisil cleanup. Chromatograms of these additional wastewaters are shown on the following pages, along with discussions about interferences in each wastewater. The chromatographic conditions were the same as in Table 29. The spiking solution used in these wastewaters was Ampul #5 (low level haloethers) of the method validation study.

Figure 3 shows the chromatogram of the blank extraction of wastewater D before Florisil cleanup. Figure 4 shows the spiked sample of the same wastewater cleaned with Florisil. The Florisil removed an interference which eluted at 11.6 minutes; this allowed

quantification of CPPE. BCEWM and BPPE have no interference problems. BCEE could be determined by blank subtraction. Only BCIPE remains undetectable at low concentrations due to interference from *bis*(chloromethyl)ethyl ether.

Figure 5 shows the chromatogram of the blank extraction of wastewater E before Florisil cleanup. Figure 6 shows a spiked sample of the same wastewater cleaned with Florisil. The interferences shown in Figure 5 obviously would prevent analyses of all five haloethers at low concentrations. Figure 6 shows that all five haloethers at low concentrations. Figure 6 shows that three of the haloethers (BCIPE, CPPE, BPPE) could easily be quantified by blank subtraction. Only the BCEE spike remains obscured by "interference"; GC/MS analysis showed this "interference" to be BCEE already in the wastewater.

Figure 7 shows the chromatogram of the blank extraction of wastewater F before Florisil cleanup. Figure 8 shows the spiked sample of the same wastewater cleaned with Florisil. Many of the wastewater compounds were removed, but only BCEE could easily be quantified. Three haloethers (BCIPE, BCEXM, and BPPE) show as shoulders on interference peaks. This suggests the possibility that a different GC program could provide enough separation to quantify these three haloethers. Only CPPE is completely masked by an interference.

Figure 9 shows the chromatogram of the blank extraction of wastewater G before Florisil cleanup. Figure 10 shows the spiked sample of the same wastewater cleaned with Florisil. Florisil removed most of the wastewater compounds, especially those eluting after five minutes. All five haloethers could be quantified, with only two of them (BCIPE, BCEE) needing blank subtraction.

Figures 11 and 12 show the chromatograms produced by wastewater H extracts. This wastewater is similar to wastewater G in that all

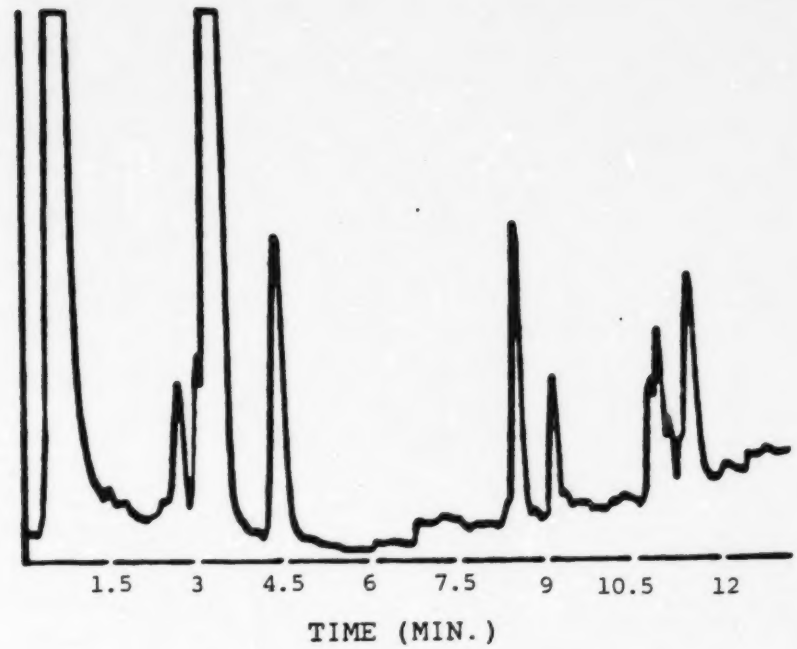

Figure 3. Chromatogram of wastewater D extract before Florisil cleanup.

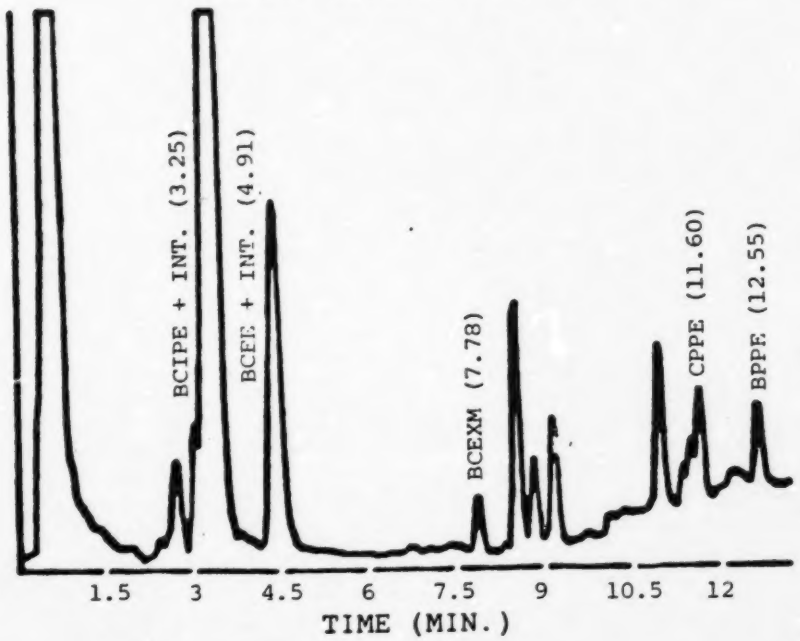

Figure 4. Chromatogram of spiked wastewater D extract after Florisil cleanup.

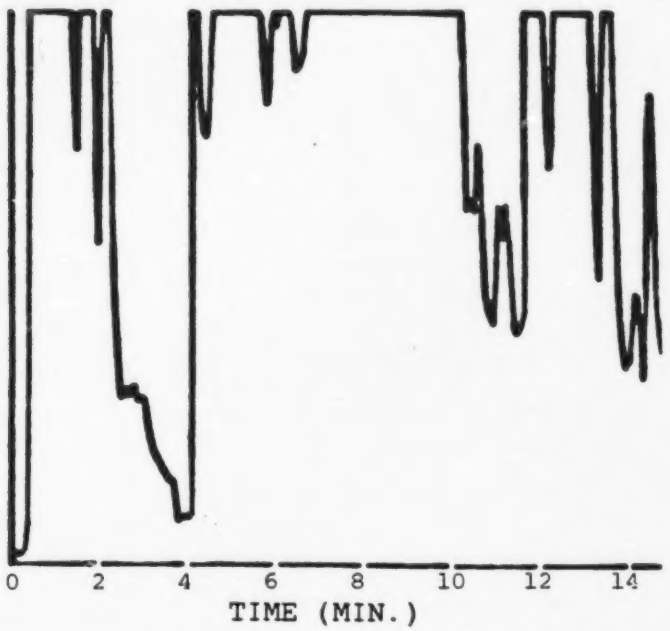

Figure 5. Chromatogram of wastewater E extract before Florisil cleanup.

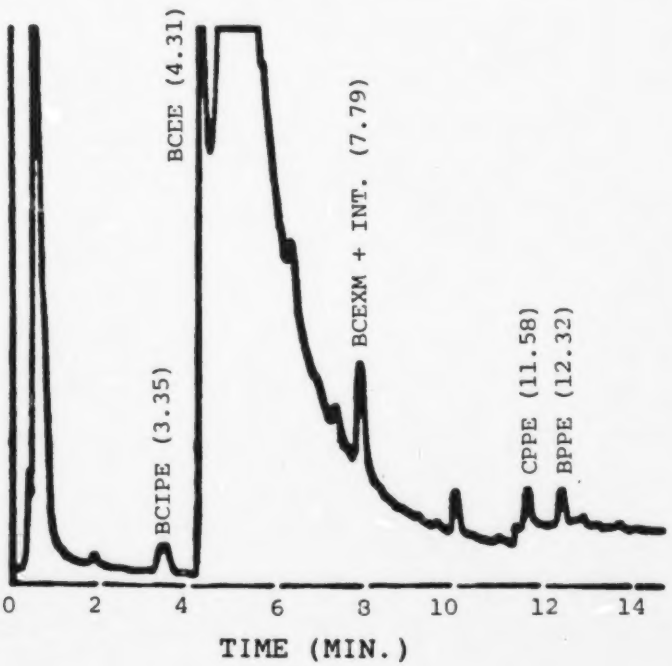

Figure 6. Chromatogram of spiked wastewater E extract after Florisil cleanup.

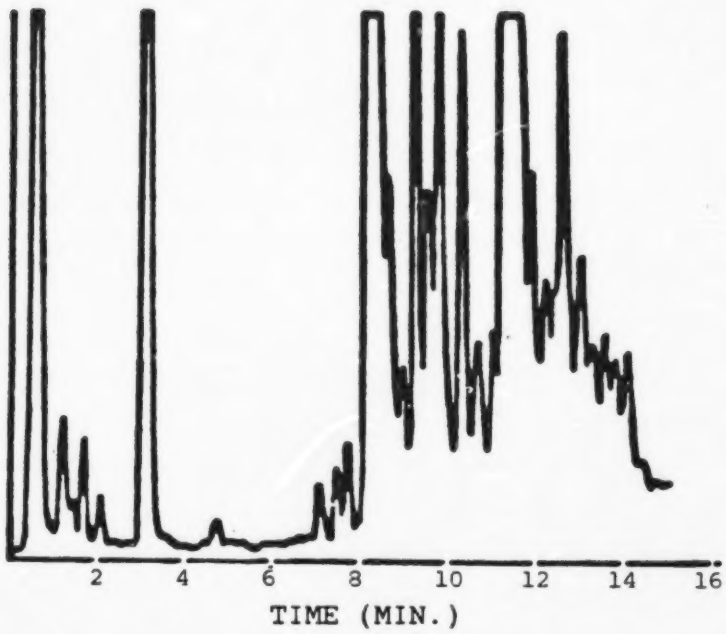

Figure 7. Chromatogram of wastewater F extract before Florisil cleanup.

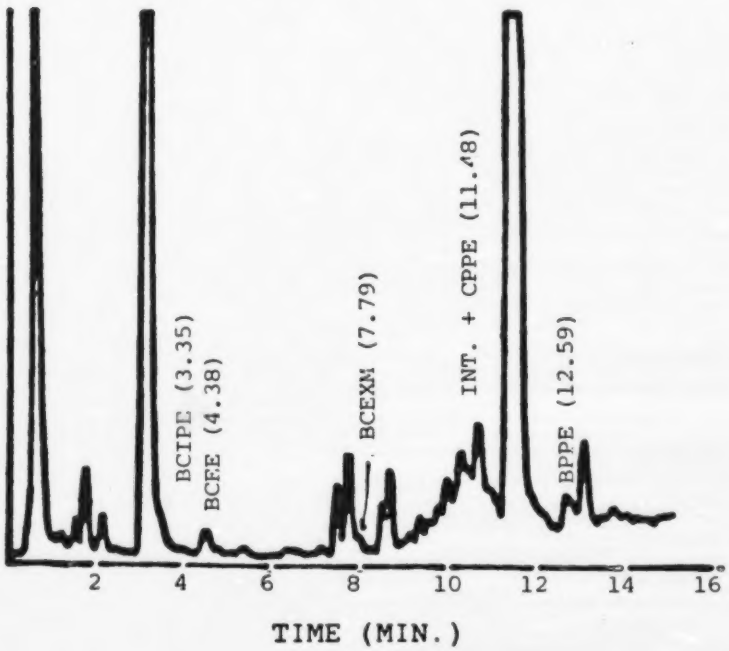

Figure 8. Chromatogram of spiked wastewater F extract after Florisil cleanup.

five haloethers could be quantified, with only BCIPE and BCEE needing blank subtraction.

Based on the results obtained with the five wastewaters discussed above, and the three wastewaters used in the method validation study, the Florisil seems to be most effective in removing compounds that elute during the last 70% of a GC analysis. Therefore, BCEXM, CPPE, and BPPE are easy to quantify even at low concentrations. Florisil was less effective on early eluting compounds, thus causing some interference with BCIPE and BCEE. However, even with these two haloethers, the concentration could usually be determined by either subtracting blank interference values or changing the GC program to effect better separation. Table 30 summarizes the effectiveness of the Florisil cleanup for each haloether in each of the eight wastewaters. This table divides the degree of interference into three classes: where the interference completely obscures the haloether peak, where the interference necessitates variation in the analytical technique to quantify the haloether concentration, and where there are no remaining interferences. It should be pointed out that these three classes are applicable only to low haloether concentrations. The interferences normally become insignificant for moderate and high haloether concentrations where less sensitive detector settings are used. A summary of interferences which are removed by Florisil, and those interferences which are not removed, is presented in Table 31.

Study of Furnace Temperature Effect

The GC/Hall detector system has many parameters that affect the sensitivity of the system for a given compound. These parameters are interrelated and each compound responds best to a different set of parameters. Since there is such a strong interrelationship among the various conditions and compounds, no single parameter can be optimized independently of the other parameters.

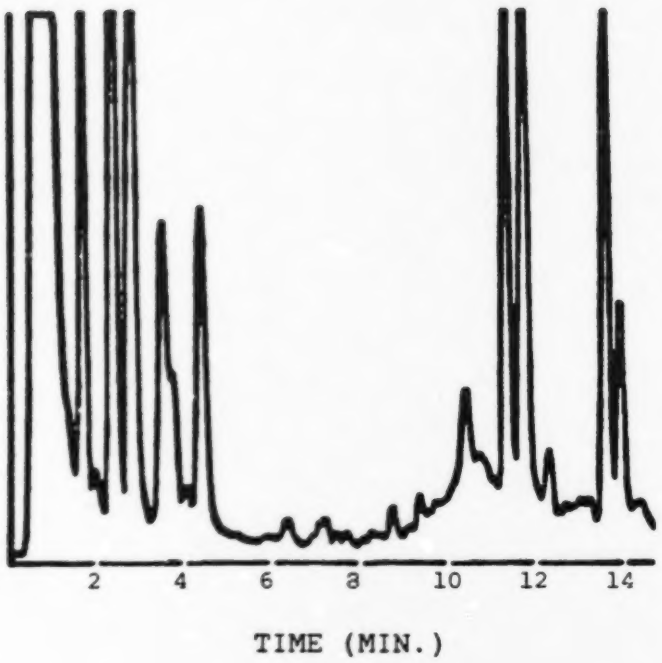

Figure 9. Chromatogram of wastewater G extract before Florisil cleanup.

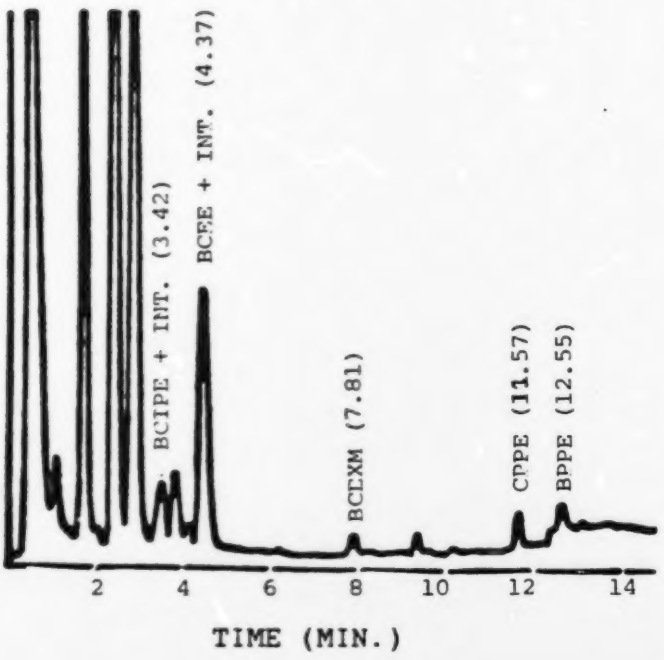

Figure 10. Chromatogram of spiked wastewater G extract after Florisil cleanup.

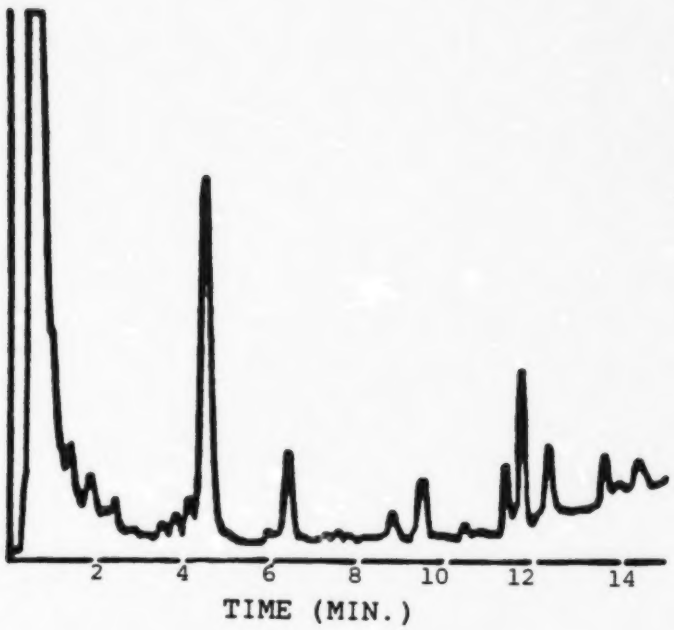

Figure 11. Chromatogram of wastewater H extract before Florisil cleanup.

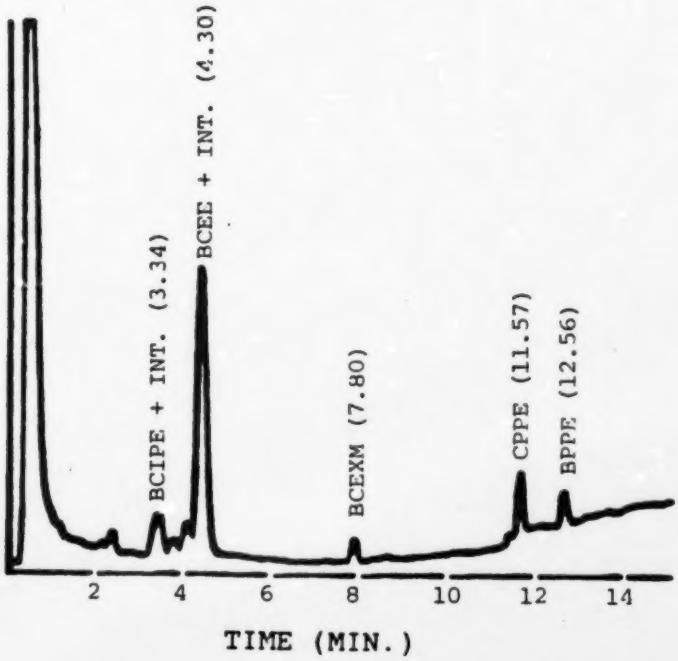

Figure 12. Chromatogram of spiked wastewater H extract after Florisil cleanup.

TABLE 30. SUMMARY OF WASTEWATER INTERFERENCES[a]

	BCIPE	BCEE	BCEXM	CPPE	BPEE
Completely obscured[b]	1	0	0	1	0
Partial interference[c]	3	4	2	1	2
No interference[d]	4	4	6	6	6

[a]The numbers in this table represent the number of wastewaters in which a given haloether falls into the described class.

[b]Low haloether concentrations are not detected due to larger interference peaks.

[c]Additional analytical steps needed to quantify haloether concentration.

[d]Haloether peak has baseline separation from interference peaks.

TABLE 31. INTERFERING COMPOUNDS IDENTIFIED BY GC/MS[a]

Haloether	RT[b]	Potential interference removed by Florisil		Potential interference not removed by Florisil	
		Name	RT[b]	Name	RT[b]
BCIPE	3.4			Hexane	0.7
				Cyclohexane[c]	2.0
				Methyl cyclohexane	2.3
				Dibromo propane[c]	3.0
				C_2-cyclopentane[c]	3.3
				Tetrachloro propane	3.4
				Bis(chloromethyl) ethyl ether	3.7
				C_2-pentane[c]	3.9
BCEE	4.3			Benzene[c]	5.0
				Toluene[c]	6.5
BCEXM	7.8	Phenyl acetate	6.3	Phenol[d]	9.7
		Butanol	7.3	C_2-Alkyl benzenes[c]	9.0-9.8
		Dichloropropanol	8.2		
		Methyl thioethyl benzene	8.4		
		Benzothiazole	9.3		
CPPE	11.6	Dipropylene glycol methyl ester	10.3	Styrene[c]	11.1
		Dimethyl malonate	11.9	Dioxothiocane[c]	11.3
		Chloro ethoxy-tolyloxy ethane	11.9		
BPPE	12.3	Tripropylene glycol	12.4	Trithiolane[c]	12.3
		Hexanol	13.6	Trithiane[c]	14.0
		Tetrapropylene glycol	14.2		

[a]Not all interfering compounds could be identified.

[b]Retention time in minutes.

[c]Seen by GC/MS and may or may not be seen by GC/Hall.

[d]Partially removed.

The delicate balance among the parameters was demonstrated during a study of reactor temperatures. The GC/Hall conditions listed in Table 29, were used except that the furnace temperature was varied during the study. One-µL injections of Ampul #5 (low concentration) were made as the furnace temperature was increased from 800°C to 880°C. The detector response was then recorded for each compound at each furnace temperature. The results are shown in Figure 13. It should be stressed that Figure 13 has true meaning only for the exact parameters and instrumentation that produced the data. Figure 13 is presented as a graphic illustration of the way each compound reacts differently to a given temperature. Even a slight change in GC/Hall conditions would drastically change the presentation of Figure 13. Some of the factors affecting response at various furnace temperatures follow:

- Transfer line temperatures
- GC column temperature program
- Electrolyte flow rate
- Electrolyte composition
- Hydrogen flow rate

Finally, the above data were generated using a Tracor Hall model 310, using a quartz reactor tube. Since the quartz tube is non-catalytic, compound response is very sensitive to temperature. The newer Tracor Hall detectors use metallic reactor tubes which contribute a catalytic effect to the reactor. This makes the reactions much less temperature sensitive and broadens the range of acceptable temperatures.

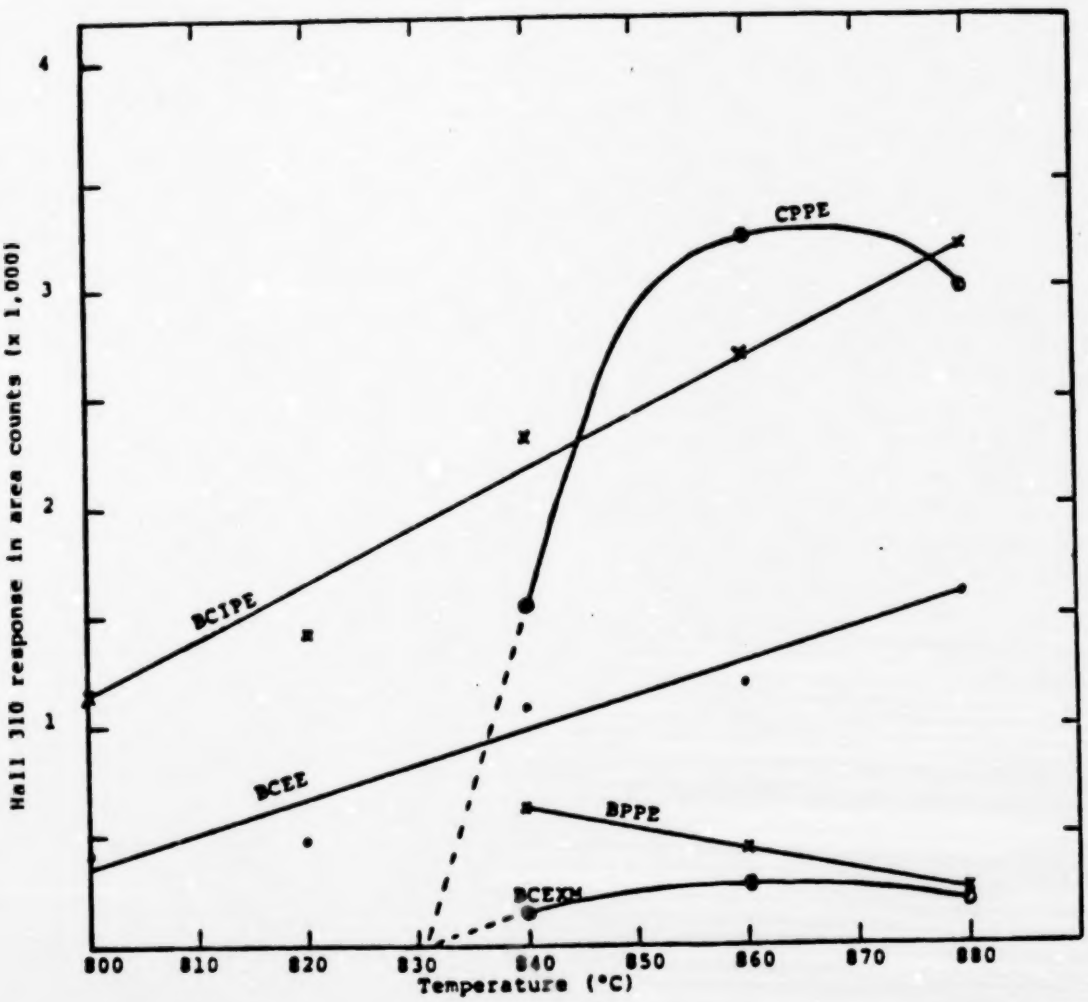

Figure 13. Hall response at various reactor temperatures.